The background of the cover is a high-resolution micrograph showing a complex pattern of ferroelectric domains. These domains appear as elongated, irregular shapes in various shades of blue and teal, separated by darker, more uniform regions. The overall texture is intricate and organic, typical of ferroelectric thin films.

INTERFACE AND DOMAIN ENGINEERING IN FERROELECTRIC BIFEO₃ THIN FILMS

ALIM SOLMAZ

**INTERFACE AND DOMAIN
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IN FERROELECTRIC
BIFEO₃ THIN FILMS**

Alim Solmaz

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Author: Alim Solmaz

Cover: Piezoresponse Force Microscopy image of 50 nm thick BiFeO₃ thin film on SrTiO₃ substrate, depicting the domains and domain walls. Designed by Alim Solmaz and Bedile Turan Solmaz.

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INTERFACE AND DOMAIN ENGINEERING IN FERROELECTRIC BIFEO₃ THIN FILMS

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus
prof.dr. T.T.M. Palstra
on account of the decision of the graduation committee,
to be publicly defended
on Friday the 31st of March 2017 at 16:45

by

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Chapter 1

Introduction and Motivation

Abstract: BiFeO₃ is one of the most important multiferroic materials that have seen a significant boost in the academic research in the last decades. Coupling between the ferroelectric and antiferromagnetic order parameters of BiFeO₃ at room temperature promises a groundbreaking technology for nano-electronic devices. Yet, there is still a need for deeper understanding of BiFeO₃ thin film growth and its functional properties. Therefore this thesis focuses on interface and domain engineering of BiFeO₃ thin films.

1.1 Introduction

Multiferroics are a very special class of materials that exhibit coexistence and inherent coupling of different primary ferroic orders such as ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidicity. Multiferroic research has a long history that goes back to the time when Pierre Curie first predicted the intrinsic coupling between ferroelectricity and ferromagnetism, i.e. magnetoelectric effect, in 1894 [1]. However, during the 20th century, the progress on theoretical and applied research of multiferroics was slow due to the poor coupling efficiency between the ferroic orders and the limited number of known multiferroic materials. The scarcity of multiferroics, especially of magnetoelectrics, is due to the contradictory requirements of ferroelectricity and ferromagnetism. Ferroelectricity requires empty d- orbitals of an ion while magnetism arises from partially filled d- orbitals of an ion [2]. One way to circumvent this problem is to find materials in which ferroelectricity and magnetism originate from different ions in a compound. In this regard, a breakthrough in multiferroic research came in 2003 by high quality thin film synthesis of BiFeO₃ (BFO) [3]. BFO is a canonical multiferroic material where the ferroelectricity arise from the 6s lone pair of Bi ion while the antiferromagnetism originates from the partially filled 3d orbitals of Fe ion [4]. In addition to being one of the rare multiferroics, BFO is also special for its critical temperatures being far above room temperature. BFO has a Curie temperature of 820 °C [5] and a Neel temperature of 370 °C [6]. Therefore the possibility of creating novel devices, which can facilitate the coupling of electric and magnetic orders at room temperature, has been the main driving force for the extensive research into BFO.

The most desired and long-sought applications of BFO are based on the magnetoelectric effect that enables the control of magnetic properties by electric field and vice versa. Using this principle, data can be written and readout in a memory device by electric and magnetic fields respectively. This brings the following advantageous: (i) data writing by electric field requires less energy in contrast to data writing with magnetic field in hard disk drives, (ii) data readout by magnetic field is a non-destructive process unlike the destructive readout by electric field in ferroelectric random access memories. Even though, the magnetoelectric effect at room temperature was shown between ferroelectric and antiferromagnetic domains of BFO thin films [7], antiferromagnetic domains are not directly useful for device applications. In order to overcome this issue, BFO was stacked with ferromagnetic Co_{0.9}Fe_{0.1} metal alloy so that an exchange bias is created at the interface. Through this exchange bias, it was possible to manipulate the magnetic state of Co_{0.9}Fe_{0.1} layer by applying an electric field to the BFO layer [8]. In addition to these magnetoelectric device applications, BFO has found applications in other fields as well. For example, one of the early applications of BFO was in non-volatile memory devices

as developed in 2006 by Fujitsu [9] using the large ferroelectric polarization of BFO. Moreover, BFO was experimented in telecommunication applications as well due to its giant terahertz radiation [10, 11]. Furthermore, abnormal photovoltaic properties of BFO [12, 13] have also revitalized the field of photoferroelectrics which essentially aims at creating devices that can harvest the solar energy.

Although multiferroic properties of BFO have been known since the 1960s [14–16], poor sample quality has obscured the progress in the field of BFO. Impurities and low crystallinity have caused extrinsic magnetic properties and high leakage currents in BFO samples, thus, have precluded the developments in BFO applications. Advances in thin film deposition techniques in the last decades have enabled the successful synthesis of BFO thin films with significantly large remnant polarization and magnetic moment [3]. These two key observations have stimulated an enormous interest in BFO in the last decades. It was later found out that the observed electrical polarization is an intrinsic property of BFO as also shown in single crystal samples [17, 18]. In contrast, later experiments failed to reproduce the observed large magnetic moment [19], and impurities were claimed to be responsible for it in Wang’s study [3]. Nowadays, it is believed that intrinsic magnetic moment of BFO is nearly zero [20].

One of the essential characteristics of ferroelectrics is the domain walls that form upon a necessity of energy minimization during sample growth. The rhombohedral crystal structure of BFO facilitates the formation of 71°, 109° and 180° domain walls¹ [21]. In the vicinity of domain walls, physical properties differ from the bulk of BFO due to changes in the crystal, charge and spin structures. For example Seidel et al. discovered domain wall conductivity in 109° and 180° domain walls of an otherwise insulating BFO film [22]. Domain wall conductivity was later shown in 71° domain walls as well [23]. Moreover, the magnitude of the exchange bias between BFO and Co_{0.9}Fe_{0.1} metal alloy was shown to scale with the length of the 109° domain walls in BFO [24]. It was further found that 109° domain walls show also a magnetoresistance effect [25]. Additionally, abnormal photovoltaic current generation in BFO was ascribed to the electrostatic potential steps at domain walls and the effect was shown to be enhanced with periodically ordered domain walls [13, 26, 27]. These emerging properties at domain walls are so striking and promising that domain walls were even considered to be utilized as the active ingredient of novel electronic devices [28].

1.2 Current challenges with BiFeO₃

BiFeO₃ is a promising material for the creation of novel nanoelectronic devices in

¹Definitions of these domain walls will be given in more detail in chapter 3.

the field of ferroelectrics, magnetism, spintronics and photovoltaics. Despite all the efforts in the research of BFO synthesis and applications, there are still unresolved issues that hamper the progress of BFO towards real device applications. Domain and domain wall ordering, origin of domain wall conductivity and leakage current problems in BFO devices stand out as the most important topics which require a deeper scientific understanding.

To utilize the domain walls as functional components in nanoelectronic devices, it is important to be able to control the types and ordering of domain walls. Several methods have been used to manipulate the domain walls in BFO such as lattice mismatch between film and substrate [29], substrate vicinality [30,31], film thickness [32], screening charges provided by electrode layers [33,34] and in-plane anisotropy of substrate surfaces [35]. Although a lot of research have addressed the growth of domain walls in BFO thin films, there are still unresolved issues such as interface effects and substrate symmetry. In recent years, oxide interfaces have become an important aspect of the thin film studies. For example, a two dimensional electron gas was discovered at the $\text{LaAlO}_3\text{-SrTiO}_3$ interface [36] and Schottky barrier change by substrate termination was reported at the $\text{SrRuO}_3\text{-SrTiO}_3$ interface [37]. Though there has been some efforts to reveal the interface effects, particularly of octahedral rotations [38], in BFO domain and domain wall growth, a complete understanding is still lacking. Therefore, interface effects on BFO domain and domain wall growth was studied in this thesis by changing the substrate termination, as presented in chapter 2.

Substrate effects on thin film growth are usually considered from the strain perspective. BFO thin films show monoclinically distorted rhombohedral [32] and super-tetragonal [29] crystal structures under low and high compressive strain, respectively. Although strain is a powerful tool for thin film engineering, it is not the only influence that a substrate can exert. Usually a rather less considered effect is the substrate symmetry. It was already shown that the number of structural variants in BFO thin films can be modulated by the symmetry mismatch on an orthorhombic substrate surface instead of the anisotropic strain exerted [39]. However, this study only considered the orthorhombic substrates with the 90° angle on the substrate surface plane. Considering that the BFO rhombohedral structure is distorted from the 90° angle on all $\{100\}$ surface planes, it is also interesting to investigate BFO growth on orthorhombic substrates that have a non- 90° angle on the surface plane. Therefore chapter 3 addresses the effects of orthorhombic substrate symmetry on BFO thin film growth.

One of the biggest impediments of actual BFO applications lies in the electrical performance of the devices. Electrical characterization of BFO structures have revealed various mechanisms to be responsible for the main electrical properties, in-

cluding bulk [40–45] and interface limited conduction mechanisms [23,46–48]. Unfortunately, there is no consensus on the main conduction mechanism in BFO structures. This is partly due to the differences in sample growth and partly due to the nature of the applied electrode materials. In order to utilize BFO in device applications, its electrical properties need to be improved, which requires an in-depth understanding of the conduction mechanisms in BFO structures. Therefore chapter 4 is dedicated to the study of conduction mechanisms in BFO, focusing on the influence of interface effects as shown in prior chapters, where interface effects play a crucial role in the structure of BFO thin films.

The discovery of 109° domain wall conductivity in BFO thin films [22] has sparked an enormous attention for more detailed investigation of domain walls in ferroelectrics. Domain wall conductivity was later shown in other domain wall types of BFO [23,47] and other ferroelectric materials such as $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (PZT) [49], LiNbO_3 [50] and hexagonal manganites [51,52]. Even though these observations have led researchers to consider domain wall conductivity as a universal phenomenon in ferroelectrics, it has not been possible to put forth a single mechanism to be responsible for the observed phenomenon. Among various mechanisms, discontinuities in the electrical potential and band gap values in the vicinity of domain walls, which are driven by the structural and polarization changes, were claimed to cause domain wall conductivity [22]. Additionally, oxygen vacancies were also shown to enhance the domain wall conductivity via thermally activated charge carriers [47,48]. Discrepancies between the claimed mechanisms are likely to be due to the way the samples were processed, resulting in structural variations. BFO is a complex oxide material whose properties are sensitive to any changes in the composition of the ions [40]. Hence it is important to have a good understanding of the influential growth parameters and be able to grow BFO thin films in a controlled way. Upon establishing a solid foundation of how the interface affects the domain and domain wall orderings in BFO thin films in chapters 2 and 3, the origin of domain wall conductivity is addressed in chapter 5. Moreover, the influence of the electrical polarization on the domain wall conductivity is an intriguing topic. Artificially created vortex-like charged domain walls in BFO thin films showed a preferential domain wall conductivity [53]. However, a proper understanding of charged domain walls and its conductivity properties is still missing in as-grown BFO thin films. This aspect of domain wall conductivity is also discussed in chapter 5.

1.3 Scope of this thesis

This thesis is focused on improving the understanding of BFO thin film growth, thus, helping to find ways to address some of the aforementioned scientific challenges in the

previous section. The approach is first to gain better control of BFO thin film growth by interface manipulation. Subsequently, electrical and domain wall conductivity properties of BFO thin films are addressed. The structure of the thesis is as follows:

- Chapter 2 describes the study of domain ordering in BFO thin films by using the SrTiO_3 substrate surface termination. Chemical treatment and interval pulsed laser deposition methods are used to obtain TiO_2 and SrO terminated SrTiO_3 substrates respectively. Piezoresponse Force Microscopy (PFM) technique is used to reveal the ordering of ferroelectric domain structures of BFO thin films.
- Chapter 3 focuses on the BFO thin film growth on orthorhombic TbScO_3 substrates. Two orientations of TbScO_3 $(110)_o$ and $(001)_o$ were used in order to investigate the substrate symmetry effects while keeping the strain constant. Structural differences of BFO thin films were revealed by using X-ray Diffraction reciprocal space map measurements and PFM.
- Chapter 4 gives a comprehensive overview of conduction mechanisms in oxide materials, especially focusing on the ferroelectric oxides. Subsequently, conduction mechanisms of BFO thin films are studied by varying the electrode and interface configurations. Two types of electrodes, namely $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and Nb:SrTiO_3 , were used in order to investigate the electrode effects on the conduction properties of BFO thin film stacks. The atomic terminating plane of the each electrode is also changed in order to investigate the interface effects deeper. Local conductivity measurements were done by Conductive Atomic Force Microscopy (C-AFM).
- Chapter 5 studies the domain wall conductivity in BFO thin films. Firstly, the origin of domain wall conductivity is discussed. Secondly, the effect of polarization changes (i.e. charged domain walls) on domain wall conductivity is given.

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Chapter 2

Domain engineering in BiFeO_3 thin films by surface termination

Abstract: Ferroelectric domain formation is an essential feature in ferroelectric thin films. These domains and domain walls can be manipulated depending on the growth conditions. In rhombohedral BiFeO_3 thin films, the ordering of the domains and the presence of specific types of domain walls play a crucial role in attaining unique ferroelectric and magnetic properties. In this chapter, controlled ordering of domains in BiFeO_3 thin films is presented. Experiments performed on two different surface terminations, namely TiO_2 terminated and SrO terminated SrTiO_3 substrates, strongly indicate that the domain selectivity is determined by the growth kinetics of the initial BiFeO_3 layers.

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2.1 Introduction

Ferroelectric, ferromagnetic and ferroelastic materials form domains when they are brought through a phase transition to a lower symmetry phase (i.e. cooled down through the Curie temperature) [1, 2]. In the case of ferroelectric thin films, the energy competition between the depolarization field and the domain wall formation energy determines the size and shape of the domains. This energy competition is governed by boundary conditions [3] such as presence of electrode layers i.e. screening charges [4] and the thickness of the films [5, 6]. In the case of ferroelastic domains, the elastic energy density, which linearly increases with increasing film thickness, needs to be balanced against the domain wall formation energy [7]. In this case, the elastic boundary conditions, such as the epitaxial strain and film thickness, determines the domain size. One of the most studied ferroelectric materials is BiFeO₃ (BFO) due to its promising multiferroic properties [8]. Intensive research has explored the relation between the growth, the domain configuration and the properties of BFO thin films [9–16] with a focus on the coupling between magnetism and ferroelectricity [17]. Even though the epitaxial strain stabilizes the monoclinic symmetry, BFO thin films remain pseudo-rhombohedral under low strain values. Rhombohedral structure facilitates that polarization lies along the $\langle 111 \rangle_{\text{pc}}$ directions, which gives rise to four structural variants and eight ferroelectric variants [1] in BFO thin films. Depending on the relative polarization directions in the adjacent domains, 71°, 109° and 180° domain walls can form with potentially different physical properties [12, 18]. The richness of domain configurations has initiated numerous studies on the influence of various aspects of the thin film growth on domain and domain wall formation such as lattice mismatch between film and substrate [19], substrate vicinality [9, 14], film thickness [15], screening charges provided by electrode layers [11, 16] and in-plane anisotropy of substrate surfaces [20].

Selectivity among the possible structural domain variants was shown by Chu et al. [21] through modification of the growth regime of a bottom SrRuO₃ (SRO) electrode layer. They observed that while an island-like multilevel growth of SRO lead to a subsequent BFO growth exhibiting four structural variants, a step flow-like growth of SRO layer limited the BFO layer to only two structural domain variants because of the symmetry breaking associated with the step edges. Moreover, Chu et al. succeeded to create as grown 71° and 109° domain walls in La-doped BFO thin films on DyScO₃ (DSO) substrates by controlling the thickness of the SRO bottom electrode layer [11]. They proposed the driving force for this selectivity to be the screening charges provided by the electrode layer. Additionally, Johann et al. carried out a systematic study on the effect of strain and electrical boundary conditions on BFO growth, pointing out that films grown on SrTiO₃ (STO) substrates with and without a SRO bottom electrode layer have different topographical and ferroelectric

properties [16]. This was attributed to the fact that STO substrate is TiO_2 terminated whereas SRO layer terminates with SrO atomic plane (due to the loss of the top RuO_2 plane which is caused by the volatility of Ru) [22]. The incorporation of a SRO electrode layer affects the growth of BFO thin films by a combined modification of the step edges, screening charges and surface termination, which has hampered the detailed analysis of the specific role of each individual factors.

In this chapter, the dependence of topographic and ferroelectric domain structures in BFO thin films grown on SrRuO_3 electrode layer with various thicknesses to investigate its effects in BFO growth was studied. Upon obtaining the results that point to a critical role of surface termination, the modification of STO surface termination and thereupon the thickness evolution of the BFO thin films on such substrates were investigated. In order to ensure the precise control over the surface termination, transmission electron microscopy (TEM) analysis of the film-substrate interface was carried out. Additionally X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the film stoichiometry and piezoresponse force microscopy (PFM) was used to determine the ferroelectric properties. It was found that the initial growth kinetics which can be controlled by modification of the STO surface termination determines the formation of ferroelectric domains and domain walls in BFO thin films.

2.2 Experimental

BFO thin films were grown by pulsed laser deposition (PLD) in a Twente Solid State Technology (TSST) system on undoped and 0.5 wt% Nb-doped STO (001) substrates, with the growth being monitored by *in-situ* reflective high-energy electron diffraction (RHEED). A combined chemical and thermal treatment was applied to achieve a single TiO_2 termination of the STO substrates [23]. On the other hand, the single-terminated SrO surfaces are obtained by deposition of a SrO monolayer on a single-terminated TiO_2 surface. For epitaxial SrO monolayer growth, pulsed laser interval deposition was applied [24]. In this technique, the total number of deposition pulses to form one monolayer was provided fast enough (50 Hz) to stabilize the SrO layer without multilevel islands. In order to achieve this, a single-crystal SrO target is ablated with an energy density of 1.3 J/cm^2 while the substrate is held at 850°C in an oxygen environment at 0.13 mbar. This results in crystalline SrO-terminated STO surfaces with perfectly straight step edges [25]. For samples with electrode layer, SrRuO_3 thin films were deposited from a SrRuO_3 target (prepared by solid state reaction method) at 600°C and 0.13 mbar O_2 pressure with an energy density of 2.0 J/cm^2 and a repetition rate of 1 Hz. Upon which the samples are heated up to 670°C at 0.3 mbar O_2 for BFO thin film growth where deposition is done from

a Bi_{1.1}FeO₃ target (i.e. 10% Bi excess, prepared by solid state reaction method) with the same energy density as of SrRuO₃ and a repetition rate of 0.5 Hz. For all depositions, the target-substrate distance was fixed at 55mm. After deposition the thin films were slowly cooled down to room temperature in 100 mbar of oxygen at a rate of 10°C/min to optimize the oxidation level.

Topographic and ferroelectric features of the samples were measured at room temperature by tapping and PFM mode, respectively, on a Bruker Dimension ICON microscope and UHV-Omicron Nanotechnology GmbH VT-AFM (modified for PFM) using Cr/Pt coated probes. XPS measurements were performed on *in-situ* prepared samples in a synthesis/analysis cluster system with pressures below 1x10⁻⁹ mbar during sample transfer to avoid any contamination. The XPS system (Omicron Nanotechnology GmbH) is equipped with a monochromatic Al K α (XM 1000) X-ray source (1486.6 eV) and an EA 125 electron analyzer was used. All spectra were acquired in the constant analyzer energy (CAE) mode. High-angle annular dark-field (HAADF), scanning transmission electron microscopy (STEM) in combination with energy-dispersive X-ray spectroscopy (EDX) was performed on an FEI X-Ant-EM electron microscope at the University of Antwerp, operated at 300kV, fitted with an aberration corrector for the probe-forming lens as well as a high-brightness gun and a highly efficient EDX detector system with a collection solid angle close to 1 Sr [26]. A convergence semi-angle of 21.0 mrad was used, providing spatial information down to 0.8 Å. Cross-sectional cuts of the samples along the [100] direction were prepared using a FEI Helios 650 dual-beam Focused Ion Beam device. Crystal structure characterization was done by an MRD X-ray diffractometer (XRD) from PANalytical.

2.3 Results and Discussion

2.3.1 Effect of SrRuO₃ electrode layer on the growth of BiFeO₃ thin films

The effect of SrRuO₃ electrode layer on the BFO thin films was investigated by varying the SrRuO₃ layer thickness from 2 unit cells (~0.8 nm) to 20 nm while keeping the thickness of the BFO thin film constant at 60 nm. The thickness of the SrRuO₃ electrode layer and BFO thin films were determined from the *in-situ* monitor by RHEED and X-ray reflectivity measurements (data not shown). Figure 2.1 shows AFM topography images (a-c) and ferroelectric domain images (e-g) of the 60 nm thick BFO thin films on SrRuO₃ electrode layers from 20 nm down to 2 unit cell height, from left to right in each row respectively. As seen in these images, topographic features as well as the ferroelectric domain structure of the BFO thin films grown on SrRuO₃

electrode layer, even for only 2 unit cell thick, are comparable to each other. However, the BFO thin film grown on a bare STO substrate shows a large difference in the topography image (d), i.e. island-like features with sharp edges, even though it possesses a similar ferroelectric structure (h) to the others. It was observed that all samples were uniformly polarized in the out-of-plane direction. For samples with SrRuO_3 layers thicker than 5 nm, the out-of-plane polarization direction of BFO is downwards, pointing towards the electrode layer, whereas for the other samples we were not able to detect the direction due to the reduced conduction of the electrode layer as the thickness decreased.¹ The preferential poling in the out-of-plane direction is common in ferroelectrics and observed earlier in BFO thin films [27] where the reason could be either due to the screening charges provided by the electrode layer and/or the accumulation of the positively charged oxygen vacancies near the surface [28, 29] during the sample growth and/or cool down in vacuum conditions. In contrast to the out-of-plane domain formation, which is mostly dictated by the electrostatic forces, the in-plane domain structure is mainly governed by the elastic forces. Even though the ferroelectric structures of the BFO thin films look similar when varying the SrRuO_3 electrode layer thickness, see Figure 2.1(e-h), there seems to be a correlation between the sharp edges on the BFO topography (d) and the ferroelectric domain boundaries (h) in the case of BFO films without SrRuO_3 layer. Therefore the effects that might be affecting the stabilization of different types of elastic structures in the BFO thin films are considered. It is noteworthy that one of the differences between the samples with and without the SrRuO_3 electrode layer is the surface termination. Bare STO substrates are singly TiO_2 terminated whereas the SrRuO_3 thin films are SrO terminated due to the Ru loss during the growth [22]. This has prompted to study the effect of the STO surface termination on the growth of the BFO thin films.

2.3.2 Surface Termination Control of SrTiO_3 Substrates

In the last decades, developments in the growth techniques enabled the atomically controlled growth of oxide thin films, thus helped to discover new physical phenomena in the oxide electronics that might enrich the physics used in the semiconductor technology in the coming years. As the device size shrinks and the films get thinner in modern electronics, the interface becomes the device as stated by Herbert Kromer in his Nobel Lecture in 2000 [30]. Even though he was putting an emphasize on the

¹PFM detects the domains (in-plane and/or out-of-plane) based on the relative phase difference in response to the drive voltage. Therefore the absolute measurement of the out-of-plane polarization is done by polarizing the sample with DC voltage from which it is possible to deduce the as grown out-of-plane polarization direction. In the absence of a conducting electrode layer, it is not possible to switch the polarization by PFM due to the low applied electric field, thus no ability to determine the direction.

Figure 2.1: (a-d) Topography images of 60 nm thick BFO thin films on STO substrates with various thicknesses of SRO electrode layers, namely 20 nm, 5 unit cells, 2 unit cells and no SRO respectively. (e-h) Corresponding PFM in-plane amplitude images in the same order as (a-d).

interfaces in semiconductor devices, oxide electronics can show remarkable new emergent phenomena as reviewed in [31]. The discovery of the two dimensional electron gas at the LaAlO₃-SrTiO₃ (LAO-STO) interface [32] has initiated numerous studies. They reported the formation of electron doped (n-type) conducting La³⁺O²⁻-Ti⁴⁺O₂²⁻ interface when LAO grown on TiO₂-terminated STO (B-site STO) surfaces whereas formation of hole doped (p-type) insulating Al³⁺O₂²⁻-Sr²⁺O²⁻ interface when LAO grown on SrO-terminated STO (A-site STO) surfaces.² This is even further investigated by Nishimura et al. [33], confirming that the coverage of SrO at the interface is a determining factor in controlling the conducting/insulating character of the interface. Even though both types of interfaces on A-site and B-site terminated STO surfaces have a polar nature in the ideal case, the fact that electrical conductivity appeared only at the n-type interface raised questions for the real nature of these interfaces. It was later claimed that at the LaO-TiO₂ interface, electronic reconstruction is the main way of charge compensation, which promotes the conducting character. On the other hand at AlO₂-SrO interface the charge compensation takes place by formation of oxygen vacancies and the atomic interface reconstruction hampers the emergence of a conducting layer [34]. These observations indicate the importance of atomic ordering at the interfaces. As the results from the Figure 2.1 point to a direction that the surface termination might be playing a dominating role in the growth of the BFO thin films, it is crucial to be able to control the surface

²A-site and B-site naming comes from the 'ABO₃' nomenclature for perovskite structures.

termination of the STO substrates.

B-site (TiO_2) termination of the STO substrates is achieved by a combination of chemical and thermal treatments [23]. To our knowledge, such a chemical treatment procedure has not been reported so far for the A-site (SrO) termination although there are several other methods available. These methods generally include thermal annealing steps at moderate temperatures ($< 900^\circ\text{C}$) [35] as well as mild ion etching procedures [36]. However these methods were reported to result in a mixture of TiO_2 and SrO species on the surface by Bachelet et al. [37]. Instead these authors proposed to exploit the diffusivity of the SrO species during thermal annealing at high temperatures ($\sim 1300^\circ\text{C}$) by which SrO terminated STO surfaces were achieved. However this treatment results in the formation of kinks at the step edges. As the step edges play an important role in the growth of the BFO thin films [14], this is not the best way to achieve SrO termination. Another well established method for achieving a SrO terminated STO surface is to deposit a single SrO layer by pulsed laser deposition or molecular beam epitaxy which requires the *real-time* monitoring of the growth.

As mentioned in the experimental section, we followed the interval deposition of SrO layer from the recipe as developed in [24]. This method requires a precise control of the deposition in *real-time* by RHEED. Figure 2.2(a) shows the RHEED intensity changes of the specular spot after the SrO layer is deposited rapidly. The plots show three different experiments for the optimization of SrO single layer deposition where the number of laser pulses applied are 30, 60 and 70. It is observed that 60 pulses under these certain circumstances (as described in the experimental section) give rise to a nearly full coverage of the surface with SrO whereas 30 and 70 pulses causes under and over coverage, respectively. 30 pulses causes a relatively smaller recovery of the intensity due to the insufficient recovery of the surface roughness. 70 pulses causes a decrease in intensity after reaching a peak point due to the excess amount of SrO species creating surface roughness. Additionally images of the RHEED spots before and after 60 pulses of SrO deposition show two dimensional surface, that means no surface roughening takes place, see Figure 2.2(b,c). These results are also cross checked with the topography measurements by AFM as shown in Figure 2.3. 30 pulses of SrO results in a surface that is covered with patches of SrO whereas 60 pulses with nearly full coverage and 70 pulses with relatively higher roughness. Therefore, we believe that in our experiments we have a good control over the STO surface termination and we can investigate the influence of the termination site on the BFO thin film growth.

Figure 2.2: (a) Plots showing the change of the specular intensity after rapid deposition of SrO layer with various pulses 30, 60 and 70, indicated by red, black and blue colors respectively. (b,c) Rheed diffraction spots before and after 60 pulses of SrO deposition, respectively.

Figure 2.3: AFM topography analysis of SrO deposition. (a,d,g) are the topography images of the bare STO substrates before SrO deposition. (b,e,h) are the topography images after SrO deposition of 30, 60 and 70 pulses respectively. (c,f,i) are the zoomed in topography images from (b,e,h) respectively.

2.3.3 BiFeO₃ thin films grown on A- and B-site SrTiO₃ surfaces

Thickness evolution of BiFeO₃ thin films

In order to gain insight into the different growth modes of BFO thin films on both types of single-terminated STO substrates, the morphology evolution of the films was studied by AFM at different thicknesses ranging from 2 to 60 nm, as shown in Figure 2.4. One of the distinctive differences between both terminations is the significantly high surface roughness for all BFO films grown on B-site STO surfaces (see Figure 2.4(a-d)). In contrast, BFO films grown on A-site STO surfaces exhibit smooth terraces separated by clear, single unit cell height steps similar to the initial substrate surface morphology (see Figure 2.4(e-h)). This strong difference in surface morphology for BFO growth on both types of surfaces indicates a large difference in nucleation and growth behavior at the initial stage of the growth. BFO thin films on B-site STO surfaces show already a clear island-like morphology at a layer thicknesses of only 2 nm, indicating a high nucleation density during initial growth as shown in Figure 2.4(a). This results in an island-like structure, which remains present for the rest of the thin film growth (see Figure 2.4(a-d)). This roughened growth of BFO is in good agreement with the results by Chinta et al. [38] where time resolved specular and diffuse X-ray scattering was used to study the growth of ultrathin BFO on B-site STO. They reported that layer-by-layer growth of BFO takes place up to a critical thickness of 2.5 unit cells and is subsequently followed by 3D island-like growth. Due to this growth behavior, they referred to the BFO/STO heteroepitaxy system as an example of Stranski-Krastanov (SK) growth, where surface roughening is associated with the elastic forces imposed by the strain mismatch between the film and the substrate.

On the other hand, for the BFO growth on A-site STO surfaces, we observed the nucleation of species on the surface terraces, followed by a step-flow growth due to surface diffusion, that will be referred to as step-flow-like growth in the remainder of this chapter. This type of growth indicates a higher surface mobility of BFO species on A-site STO surface as compared to B-site STO surface. Additionally, this also proves that the BFO thin film growth on STO cannot be considered as a typical example of SK growth. As the crystal structure of the substrate is not altered by a change in termination and, thus, the strain applied by the substrate on the film should be similar in both cases. This rules out the strain mismatch as driving force for the surface roughening observed on the B-site terminated STO. This BFO growth behavior resembles the growth of SRO thin films on different surface terminations [22, 39] although the actual origin of the diffusivity difference of BFO species on different surface terminations is not yet known.

Figure 2.4: Topography evolution of BFO thin films with thicknesses from 2 nm to 60 nm on TiO₂-terminated (a-d) and SrO-terminated (e-h) STO (001) substrates.

Interface Investigation by TEM

In order to confirm the exact atomic termination sequence at the film-substrate interface, HAADF-STEM with EDX mapping down to the atomic scale was performed. Atomically resolved HAADF images display the presence of sharp interfaces between the BFO thin films for both B-site and A-site STO substrates, as shown in Figure 2.5(a,c), respectively. The stacking sequence of the atomic planes near the interface is directly evidenced by atomic resolution EDX elemental mapping of Bi, Fe, Sr, and Ti as presented in Figure 2.5(b,d). From these maps the final Ti (pink) and Sr (blue) terminating planes of the substrate are indicated. For clarity, the corresponding chemical line profiles taken across the film-substrate interface (see Figure 2.5(e,f)) confirm the successful control of the surface termination (indicated by vertical black arrows) achieved by a combination of chemical treatment, in order to obtain TiO₂ termination, and subsequent interval deposition, in order to create a final SrO-termination at the STO surface. Comparison of these profiles shows the presence of Ti/Fe, Sr/Bi interdiffusion over one unit cell on the B and A site respectively at the film/substrate interface (marked with (*)). As expected for epitaxial growth of perovskite (ABO₃) heterostructures, the AO-BO₂ stacking sequence is preserved at the interface and continues uninterrupted into the BFO growing film.

Stoichiometry determination by XPS

Possible volatility of Bi species might be the cause of a non-stoichiometric growth in the initial stage, thereby partially obstructing the BFO growth on B-site STO. XPS measurements were performed in order to determine the exact stoichiometry of the films. To obtain information from the film-substrate interface, only 4 unit cell thick BFO films were grown, as XPS is a very surface sensitive technique. Figure 2.6 shows the XPS spectra acquired for such 4 u.c. BFO thin films on both B-site terminated (blue) and A-site terminated (red) Nb-doped STO (001) substrates, respectively. A Shirley background was subtracted and the peaks were aligned using the O 1s peak at

Figure 2.5: Atomically resolved HAADF-STEM images (a,c) and its corresponding EDX elemental maps (b,d) of the film-substrate interface for the 60 nm thick BFO film grown on TiO₂ and SrO terminated STO (001) substrates, respectively. Chemical line profiles across the interface for elemental composition is plotted in (e,f), the vertical arrows indicate the interfaces between the BiO-TiO₂ atomic planes (green-pink) and SrO-FeO₂ atomic planes (red-blue) for BFO grown on both TiO₂ and SrO terminated STO substrates, respectively.

530.1 eV as an energy reference position. At first sight, the difference in ratio between the Bi 4p_{3/2} peaks with respect to the Fe 2p_{1/2} and Fe 2p_{3/2} peaks for both samples, indicates a different elemental composition. The concentration of the elements in these thin films was calculated through a comparison of the integrated peak area. For the bismuth concentration, the Bi 4p_{3/2} peak is fitted with a curve with respect to Bi 4f_{5/2} and 4f_{7/2} peaks (data not shown here) taken as reference peaks as the Bi peak is well defined in this range. For the iron concentration, the area under the Fe 2p_{1/2} and Fe 2p_{3/2} peaks was taken into account as these are the only peaks with strong enough intensity and no contribution from nearby Auger peaks (as this is the case for Fe 2s) which could hamper a proper background subtraction. Comparison of integrated peak areas (normalized with their respective relative sensitivity factor) estimates a concentration distribution of 54% Fe - 46% Bi and 44% Fe - 56% Bi in the BFO films grown on B-site and A-site STO substrates, respectively. However, for such ordered perovskite layers with well-defined atomic stacking layers, the difference in position of the equivalent atomic planes relative to the surface has to be taken into consideration to moderate this conclusion. In the case of BFO on A-site STO, as shown in the schematic of Figure 2.6, the BiO atomic planes are half a unit cell shifted towards the surface with respect to the FeO₂ atomic planes. It is known that the probability of electrons escaping from a material decreases exponentially with

the relation between the growth behavior and the ferroelectric properties are considered for further investigation. Since BFO thin films were grown in the ferroelectric phase, i.e. below the Curie temperature, under ideal conditions, all four structural variants are equally favorable to be stabilized during growth. However, as reported before, the substrate vicinality [9,14] or the growth regime of the underlying bottom electrode layer [21] can cause a selectivity among these structural variants leading to a selectivity in the ferroelectric domains. Figure 2.7 shows the topography and in-plane PFM images of 60 nm thick BFO thin films grown on A-site and B-site STO substrates. Note that both films have uniform polarization in the out-of-plane direction, thus no contrast appear in the out-of-plane PFM phase image (data not shown). In both cases, the ferroelectric domains form different patterns and contain a different number of structural variants, as can be seen on Figure 2.7(b,d). On B-site STO surfaces, the BFO film exhibits smaller domains of four structural variants. Furthermore, sharp features on the topography also appear to act as pinning sites for the ferroelectric domains. Existence of four structural variants in these films can be deduced from the PFM phase image consisting of more than two contrast levels (color coded as yellow, light-brown, dark-brown and brown) as well as reciprocal space mapping by XRD (data not shown here). This domain formation is attributed to the limited mobility of BFO species on B-site STO surfaces. Detailed PFM analysis [44] reveals that between these equivalent structural variants, 71° domain walls are predominant, in good agreement with previous studies [9].

On the other hand, as shown in Figure 2.7(c), BFO films on A-site STO (001) substrates exhibit a reduced nucleation density and a step flow-like growth, resulting in the selectivity of only two structural variants. This is reported to be due to a suppression of the distortion of these BFO structures as a consequence of the elastic constraints imposed by the cubic unit cell of the substrate to the film. [14] Additionally, BFO films on A-site STO substrates show very long domains with well-ordered 71° domain walls as shown in Figure 2.8. The superposition of topography and PFM images for the selected area shown in Figure 2.8 reveals a correlation between the end points of the domains and the location of defects at the surface of the film. This might be due to two possible reasons: the first one is that two domains with an orientation difference of 109° nucleate simultaneously and grow towards each other. Due to the elastic incompatibility at such domain walls, at the meeting point a defect might be created to release the strain energy associated with it. The second one is that any disorder on the initial surface of the substrate can cause a defect point because of imperfect SrO monolayer coverage. The existence of other defect points, which are not necessarily located at 109° domain walls in the film, suggests that the second reason is more likely to happen in this system.

Figure 2.7: Topography (a,c) and PFM in-plane phase (b,d) images of 60 nm thick BFO thin films grown on TiO_2 -terminated and SrO-terminated STO (001) respectively.

Figure 2.8: (a) Topography and (b) PFM in-plane phase images of 60 nm thick BFO film grown on SrO-terminated STO (001), featuring $20 \times 20 \mu\text{m}^2$. Inset in (b) is the superposition of the topography and phase images showing the coincidence of the end points of domains with the defects in the film.

2.4 Conclusion

In this chapter, the growth of BFO thin films on A- and B- site terminated STO substrates was investigated. Control over the termination site of the substrate changes the growth kinetics of BFO thin films. On B-site STO, growth takes place with high nucleation density and all four structural variants of BFO are present in the film. On the other hand, A-site STO leads to a step flow-like growth of BFO and promotes the species to reach the step edges so that it creates selectivity among the structural variants with well-ordered domains. These results open a route to investigate the effects of growth kinetics for BFO thin films on other substrates as well. In the next chapter the BFO growth on TbScO₃ substrates with and without single SrO layer on the substrate surface will be discussed.

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Chapter 3

Tuning domain walls in BiFeO_3 thin films on TbScO_3 substrates

Abstract: BiFeO_3 thin films, grown under a low epitaxial strain, have a monoclinically distorted pseudocubic crystal structure. This distortion from the ideal cubic structure results in the formation of elastic domains. Two questions are addressed in this chapter. First question is whether the substrate symmetry can be exploited in order to manipulate the ferroelectric/ferroelastic domains in BiFeO_3 thin films. This is studied by using $(110)_o$ and $(001)_o$ cut TbScO_3 substrates. It is found that a change in the symmetry of the substrate can stabilize different structural variants in BiFeO_3 thin films. Second question is what the role of the growth kinetics is for BiFeO_3 thin films grown on TbScO_3 substrates. It is found that a controlled selectivity between the 71° and 109° domain walls can be achieved by growth kinetics which can be changed by substrate surface termination. In this chapter, it is shown that both substrate symmetry and growth kinetics are crucial factors for BiFeO_3 thin film growth and orthorhombic TbScO_3 substrate provides a very rich playground to discover this.

3.1 Introduction

The developments in the growth of oxide thin films enabled the growth of high quality epitaxial thin films and provided a very rich playground where strain and symmetry mismatch between the film and the substrate can be exploited to achieve new exotic phenomenas that do not exist in the bulk form [1–4]. As the ferroelectric and anti-ferromagnetic properties of BiFeO₃ (BFO) strongly depend on its crystal structure, strain engineering has been extensively explored in the growth of BFO in order to fine tune its properties. Below the Curie temperature (~ 1100 K), bulk BFO has a rhombohedral symmetry that can be reduced to several lower symmetry structures when grown under appropriate strain conditions. As a result of the large degree of freedom in the structure of BFO with the flexibility in the cation displacement as well as the adaptability of oxygen octahedral tilts, BFO can accommodate large compressive strains (up to $\sim 4.5\%$) as well as tensile strains ($\sim 1.1\%$)¹ [5]. As depicted in Figure 3.1, BFO thin films can have crystal structures from tetragonal symmetry to orthorhombic symmetry. Large compressive strain results in coexistence of tetragonal-like and rhombohedral-like structures with coherent boundaries, which is also referred to as a super-tetragonal phase [6]. Formation of the super-tetragonal phase is regarded as a strain driven morphotropic phase in analogy to the morphotropic phase boundary (MPB) found in the lead-zirconate-titanate (PZT) system. The discovery of a MPB phase in BFO thin films, grown on LaAlO₃ (LAO) substrates, drew a significant attention due to the promising properties such as large polarization values around ~ 150 $\mu\text{C}/\text{cm}^2$ [7] and giant electroresistance values (OFF/ON ratio ~ 10000) [8]. BFO thin films grown under low compressive strains ($< 1.5 - 2\%$) show a monoclinically distorted rhombohedral structure (M_A) as shown in Figure 3.1, also referred as R-like phase. This phase is usually formed when BFO thin films are grown on substrates such as SrTiO₃ (STO) [9], DyScO₃ (DSO) [10] and TbScO₃ (TSO) [11]. Due to the dominant use of STO substrates in the field of oxide thin films, R-like phase is also the most extensively studied form of the BFO crystal structure. On the other hand, BFO thin films grown under tensile strain are probably the least understood and studied BFO crystal structure form [5] and it stabilizes an orthorhombic phase of the BFO crystal structure [12].

Among the rich crystal structures that BFO thin films can exhibit, the R-like phase has a special importance as it can allow the formation of different types of ferroelastic and ferroelectric 71° , 109° and purely ferroelectric 180° domain walls. Figure 3.2(a) represents the unit cell structure of the R-like BFO phase when grown under low compressive strain conditions. Due to the octahedral distortions, pseudocubic BFO unit cell has a tilted structure with respect to the perfect cubic unit cell. This

¹The maximum tensile strain that can be applied was limited due to the range of commercially available substrates.

Figure 3.1: Crystal structures that can form in BFO thin films under various strain conditions. Reproduced from Ref. [13]

results in the formation of four possible structural variants, named R_1 to R_4 . The polarization lies along the longest axis (one of the $\{111\}$ directions) in the distorted unit cell with two possible out-of-plane directions. Therefore, potentially eight polarization variants can be present in R-like BFO thin films. Representative definitions of the domain walls are given in Figure 3.2(b) where the naming comes from the angle between the polarization vectors. Another way to recognize the type of domain walls is to look at the change in the polarization vector between the adjacent domains. If the polarization vector changes only in one cartesian axis, as an example shown in the figure from $[11\bar{1}]$ to $[111]$, it is called 71° domain wall. Similarly, if it changes in two or three directions, the domain wall is named 109° or 180° respectively. 71° and 109° domain walls (ferroelastic and ferroelectric) require a structural transition between the adjacent domains, thus, might cause emergence of localized new physical properties that do not exist in the bulk of the thin films i.e. within the domains [14, 15]. Therefore it is important to have good control over the realization of specific domain walls.

BFO thin films grown on STO typically show 71° domain walls with some regions of 109° domain walls, as shown in chapter 2 and Ref. [9]. TSO $(110)_o$ substrates prompts the formation of 109° domain walls in BFO thin films, which is attributed to the anisotropic surface plane of the substrate [11]. Moreover, Chu et al. succeeded to create as grown 71° and 109° domain walls in La-doped BFO thin films on DSO $(110)_o$ substrates by controlling the thickness of the SRO bottom electrode layer [10]. They proposed the driving force for this selectivity to be the screening charges provided by the electrode layer. Actually this is a very intriguing observation as the role of the screening charges and the depolarization field in ferroelectric thin films have been a very controversial issue in the last couple of decades. In the 1970's, Batra and Silverman at IBM published theoretical calculations for the effects of depolarization field on the thermodynamical stability of ferroelectrics and claimed that below a certain thickness, the depolarization field will prevent the ferroelectric order in thin

films [16]. This was even claimed to be the reason why IBM has stopped working on the ferroelectric memories in those years [17]. This shows the importance of understanding the role of the depolarization field in the physics of ferroelectrics.

A depolarization field arises due to uncompensated polarization charges in ferroelectric thin films, thus, it is one of the main driving forces for domain formation. In line with the requirements of modern electronics, there is a demand to explore the properties of ferroelectric thin films with thicknesses smaller than 100 nm and even down to only several unit cells thick. This has also initiated discussions on dead layers, where the film does not act as a ferroelectric layer anymore [18–21]. Additionally, Dawber et al. [22] revised the model regarding the relation between the coercive electric field and the film thickness by modifying the corrections of the depolarization field. This shed new light on the influence of the screening charges provided by the electrode layers on the ferroelectric thin films as well as emphasized the importance of the selection of the suitable electrode layers. Later it was shown that by careful control of the depolarization field, it is possible to modify the nanodomain structures in ferroelectric thin films [23]. The aforementioned examples give some insight into the role of the depolarization field in the ferroelectric thin films and in this respect, the study of Chu et al. [10] appears to be an important one as the screening charges are held to be responsible for the selectivity between 71° and 109° domain walls in the BFO thin films. In order to clarify the differences between samples that exhibit 71° and 109° domain walls, the schematics for unit cell structures forming the films and the directions of the domain walls are shown in Figure 3.3 with representative topography images, taken from Ref. [10]. A significant difference between these type of domain walls is that 71° domain walls form parallel to the (101)_c plane whereas 109° domain walls are parallel to either (010)_c or (100)_c planes [24] due to the elastic boundary conditions. Moreover, BFO thin films with 71° domain walls have smooth surfaces with only unit cell height step differences that comes from the miscut of the substrate. On the contrary, formation of the 109° domain walls requires the tilting of the (001)_c planes in the BFO unit cell structures with respect to the substrate, hence results in the puckering of the surface as shown in the topography image. Additionally, for the domain walls to preserve charge neutrality, head-to-tail and tail-to-head alignment of the polarization vectors is required, which dictates the altering of the polarization in the out-of-plane direction of the surface between the adjacent domains. However, in other studies, also the existence of charged domain walls is reported by transmission electron microscopy in similar samples [25].

Another point of view for the formation of 109° domain walls in BFO thin films is the anisotropic in-plane strain exerted by the TSO (110)_o substrates as put forth by Folkman et al. [11]. They proposed that the difference in elastic forces in the in-plane direction of the substrate results in the selectivity for two structural variants

Figure 3.2: (a) Schematic representation for the possible unit cell structures for R-like phase BFO grown under low mismatch strain conditions. Structural variants are named R_1 to R_4 . (b) Representative definitions of the type of domain walls are given in the schematic. For a change in the polarization vector in one, two or three Cartesian axes, the domain walls are named 71° , 109° and 180° respectively. Note that domain wall naming comes from the angle between the polarization vectors in the adjacent domains. Polarization directions chosen in this schematic is only for the representative purposes. There are other options that can also give rise to such domain walls. (b) is reproduced from Ref. [26]

Figure 3.3: (a,d) 3D representations of the structural variants that form 109° and 71° domain walls, respectively. (b,e) Depiction of the domains and the domain walls and (c,f) typical AFM topography images of BFO thin films with 109° and 71° domain walls respectively. (c,f) reproduced from Ref. [10]

among the four possible variants. However, this idea was challenged by Chen et al. [27] where they studied the growth of BFO thin films on DSO (110)_o substrates by incorporating a thin layer of STO between the substrate and the BFO film. They reported that the STO layer changes the symmetry of the surface (associated with the octahedral tilts) while keeping the in-plane anisotropy intact. As a result, selectivity for two variants was attributed to the substrate symmetry, which was claimed to be transferred to the film through octahedral tilts, instead of the anisotropic in-plane lattice of the substrate. It is noteworthy to mention that in Chen et al.'s study they only observed 71° type of domain walls with and without the STO layer. This points out the variations observed in the growth of BFO thin films, thus, emphasizes the need for more elaboration for BFO thin film growth on orthorhombic substrates.

In this chapter, the substrate symmetry effect on BFO thin films is investigated by using orthorhombic TSO (110)_o and TSO (001)_o substrates. Among these substrates, TSO (110)_o has anisotropic in-plane lattice constants with the crystal axes are perpendicular on the surface plane whereas TSO (001)_o have equal in-plane lattice constants with crystal axes crossing at an angle different than 90° on the surface plane. These differences on the substrate surface plane are studied to reveal how they can affect the stabilization of different BFO structural variants in thin films. In addition to substrate symmetry effect, growth kinetics is also addressed for BFO thin film growth on TSO substrates. As shown in chapter 2, growth kinetics can be controlled by substrate surface termination. In order to achieve this single SrO layer is deposited on TSO (110)_o and TSO (001)_o substrates. The differences between the samples are revealed by studying the surface morphology, the sizes of the domains and the crystal structures of the films.

3.2 Experimental

TSO (110)_o and (001)_o substrates were treated to achieve single ScO₂ (B-site) terminated surfaces, in the same manner as reported for DSO (110)_o substrates [28] which is annealing the substrates at 1050 °C for 4 hours followed by a chemical wet etching in 12 M NaOH-deionized (DI) water solution for 2 hours with a subsequent treatment in 1 M NaOH-DI water solution for 30 min. This treatment was developed by exploiting the reactivity difference in Dy and Sc atoms due to their coordination numbers in perovskite structure. As the lanthanoids are expected to behave in a similar way, the proposed treatment also works for TSO substrates. However, BFO thin film growth on annealed TSO substrates with and without chemical treatment gave comparable results in our experiments.² Therefore, the results shown in this

²Annealed TSO substrates were observed to mostly have B-site termination as no indications for mixed termination was recognizable by AFM after annealing process.

chapter are of BFO films grown on B-site terminated TSO substrates that were obtained by annealing without chemical treatment. The corresponding A-site surface termination was achieved by depositing a single SrO layer in a similar way as described in chapter 2. BFO thin film growth on TSO (110)_o substrates was done using the recipe from chapter 2. For BFO thin films on TSO (001)_o substrates, two growth recipes were used. First recipe is the same as that is used for growth on TSO (110)_o substrates. Second recipe is that the deposition is done from a stoichiometric BFO polycrystalline target under 0.3 mbar O₂ pressure with an energy density of 3.2 J/cm² and repetition of 1 Hz at 670°C. Both recipes gave comparable samples regarding the structural and ferroelectric properties.³ For PFM switching analysis of BFO thin films, an LSMO layer was used as a bottom electrode. LSMO thin films were deposited under an oxygen pressure of 0.24 mbar with a laser repetition rate of 1 Hz and the energy density of 3.2 J/cm² at the temperature of 670°C with the target-substrate distance of 55 mm.

3.3 Results and Discussion

3.3.1 The symmetry effect for BiFeO₃ growth on TbScO₃ substrates

Orthorhombic substrates provide a rich playground for the investigation of symmetry effect as they can have two crystal orientations that can be used as a pseudo-cubic (pc) (001)_{pc} surface plane. For TSO (110)_o cut, the surface is an anisotropic plane with a small difference in the in-plane lattice constants of 3.9530 Å and 3.9570 Å where the γ angle is 90° as shown in Figure 3.4. On the other hand, TSO (001)_o allows to have an isotropic surface plane with in-plane lattice constants of 3.9530 Å where the α being an obtuse angle at $\sim 92.7^\circ$. This difference was previously shown to be significant for properties of epitaxially grown oxide thin films [29]. Therefore the substrate symmetry effect on BFO thin films will be studied in this chapter using TSO substrates that have a very low mismatch ($< 0.3\%$) with the film.

BiFeO₃ on TbScO₃ (110)_o substrates

In BFO thin films, ferroelectric properties are strongly linked to the structural properties as the polarization direction is coupled to the distortion of the unit cell struc-

³The second recipe was developed due to the following reason. Upon a new UV laser source was started to be used in deposition of BFO thin films with the first recipe, some contamination particles were found on the surface after deposition. This problem was solved by slight modifications in BFO growth recipe i.e. instead of an Bi excess BFO target, a stoichiometric BFO target was used with higher energy density and laser repetition rate. The details of how the laser light effects the ablation from the BFO target is yet to be discovered.

Figure 3.4: (a,b) Schematic representation of the pseudocubic unit cell within the orthorhombic unit cell where crystal directions are given in pseudo-cubic and orthorhombic indices. Reproduced from Ref. [30]. (c) Chart gives the relationship between the pseudo-cubic and orthorhombic vectors that is used in the rest of the chapter for conversions between the pseudo-cubic and orthorhombic indices.

ture. Therefore the structural analysis by X-ray Diffraction (XRD) of the BFO thin films on TSO (110)_o substrates is provided first, subsequently followed by piezoresponse force microscopy (PFM) characterization in order to reveal the types of ferroelectric domains and domain walls.

Figure 3.5(1a-1f) summarizes the XRD reciprocal space map (RSM) measurements of a 60 nm thick BFO thin film grown on B-site TSO (110)_o substrate. The results of these measurements in step-by-step order:

- ◇ (1a) and (1b) are the (004)_{pc} (in orthorhombic indices (440)_o⁴) plane maps where the diffraction plane is along the $[1-10]_o$ ($[010]_{pc}$ when $\phi = 0^\circ$) and $[001]_o$ ($[100]_{pc}$ when $\phi = 90^\circ$) crystal directions respectively.
 - In (1a) map, one intense peak means that (004)_{pc} plane of the BFO unit cell structures is parallel to that of the substrate along the $[1-10]_o$ direction.
 - In (1b) map, split into two peaks reveals that the (004)_{pc} plane of the BFO unit cell structures is tilted with respect to that of the substrate along the $[001]_o$ direction. Tilting of the (001)_{pc} film plane is proposed to be the reason for the formation of puckered surface as mentioned in the introduction [10].
- ◇ (1c) and (1d) are the (103)_{pc} plane family maps. In orthorhombic indices (420)_o and (33-2)_o maps where the diffraction plane is along the $[1-10]_o$ ($[010]_{pc}$ when $\phi = 0^\circ$) and $[001]_o$ ($[100]_{pc}$ when $\phi = 90^\circ$) crystal directions respectively.
 - In (1c) map, the crystal planes with the α angle⁵ are probed. The fact that there is only one peak in the (420)_o map means that BFO structural variants

⁴Please refer to Figure 3.4 for conversion rules between the orthorhombic and pseudo-cubic indices.

⁵Please refer to Figure 3.4 for the definition of the angles.

Figure 3.5: XRD reciprocal space map (RSM) results of the samples (1) BFO / TSO (110)₀, (2) BFO / SrO / TSO (110)₀ and (3) BFO / SrO / TSO (001)₀. Each map is labeled with the plane notation. Azimuthal ϕ angle, along which the diffraction plane is aligned, is noted at the bottom of each column.

with only the same (103)_{pc} plane, with respect to the [1-10]_o, direction do exist in this film. This can be realized if there is a preference for the R₁-R₂ pair (assuming they share the same α angle which is different than for R₃-R₄ pair) rather than the R₃-R₄ pair.⁶

- In (1d) map, the crystal planes with the β angle are probed. On the contrary to (420)_o map, (33-2)_o map shows two split peaks for the BFO structures with different β angles in the sample. This is in agreement with the fact that R₁ and R₂ structural variants are tilted in the opposite azimuthal directions along the [001]_o crystal axis (i.e. in the clockwise and anti-clockwise directions, respectively).
- ◇ (1e) and (1f) are the maps for (113)_{pc} plane family, in orthorhombic indices (422)_o and (242)_o when the diffraction plane is along [1-11]_o ([110]_{pc} when $\phi = 45^\circ$) and [-111]_o ([1-10]_{pc} when $\phi = 135^\circ$) crystal directions, respectively.
- In both (1e) and (1f), two split peaks are observed. Among all four structural variants, R₁+R₄ and R₂+R₃ pairs give peaks at different locations in (113)_{pc} maps. In this respect, (1e) and (1f) maps confirm the findings from (1c) and (1d) maps.
- From (1a-1f) RSM measurements, we conclude that only R₁ and R₂ structural variants with tilted (001)_{pc} surface planes do exist in the BFO thin film on TSO (110)_o substrate.

Using the full set of the map scans, the lattice constants and the angles are calculated and the results are reported in Table 3.1. For the BFO thin film on TSO (110)_o substrate, it shows that the film is strained to the substrate and the α angle is nearly the same for two structural variants. Moreover, comparing the α angles of the film ($\sim 90.50^\circ$) and the substrate ($\sim 92.76^\circ$) reveals that the substrate exerts a force on the film so that the film structures are tilted in the same direction as the substrate and tilting towards the opposite direction is prevented, see Figure 3.6 for the schematic representation. This result is in agreement with the study of Chen et al. [27] on DSO substrates where they claimed that α tilting of the substrate is transferred to the film through the octahedral rotations, causing a selectivity for two structural variants among the four possible structural variants in the BFO thin film.

Having found that only R₁ and R₂ variants exist in the BFO thin film on TSO (110)_o substrate, interpretation of the PFM results can be done more straightforward for determination of the domain wall types. Figure 3.7 shows the AFM and PFM images of a 60 nm thick BFO thin film where (a&e) are the topography images at

⁶Please refer to Figure 3.2 for the naming of the structural variants.

		a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
BFO / TSO (110) _o	TSO	3.96	3.96	3.96	92.76	89.95	89.93
	BFO R ₁	3.96	3.96	3.97	90.50	90.13	89.94
	BFO R ₂	3.97	3.96	3.97	90.49	89.79	89.94
BFO / SrO / TSO (110) _o	TSO	3.96	3.95	3.96	92.68	90.00	90.00
	BFO R ₁	3.96	3.95	3.97	89.41	90.55	90.19
	BFO R ₂	3.97	3.96	3.97	90.47	89.49	90.26
	BFO R ₃	3.97	3.96	3.97	90.48	90.51	89.74
	BFO R ₄	3.96	3.95	3.97	89.42	89.45	89.79
BFO / SrO / TSO (001) _o	TSO	3.95	3.96	3.96	92.65	89.96	90.01
	BFO R ₁	3.94	3.99	3.96	91.56	90.32	90.38
	BFO R ₄	3.94	3.99	3.96	91.56	89.60	89.64

Table 3.1: Table showing the calculated crystal parameters for the substrates and the films from the RSM measurements in Figure 3.5. Sample identities are given on the left edge of the table.

Figure 3.6: Schematic representations of the BFO thin film on TSO (110)_o substrate from the side views. (a) is along the $[1-10]_o$ crystal axis, indicating that α angle distortion in the substrate results in the BFO structures that are tilted in the same direction. (b) is along the $[001]_o$ crystal axis, showing that β angle does not cause any preferential tilting in the BFO structures.

different scan sizes, featuring the puckered surface as also reported in other studies [10,11]. (b&f) are the out-of-plane and in-plane amplitude PFM images, respectively. Amplitude images give information about the magnitude of the polarization. If the cantilever is aligned perfectly along the crystal axis, projections of the polarization vectors in adjacent domains would be exactly the same. However, this can hardly be done in experimental conditions and slight differences can arise in the amplitude image between the domains. Moreover, only at the domain walls the signal is zero because there is no response to the excitation voltage. On the other hand, phase differences in the PFM images arise due to differences in the response of the domains based on the polarization direction. Thus, PFM phase images give information about the orientation of the polarization in the film. Figure 3.7(c&g) show the out-of-plane and in-plane phase images with the zoomed-in areas in (d&h), respectively. In order to be able to identify the polarization vector for each pixel, a mask is applied in each image (d&h) by assigning different numerical values. Using MATLAB these mask images are concatenated, resulting in Figure 3.7(i). This image is the depiction of all the present domains in this sample with a color coding for polarization vectors. According to the definitions given in Figure 3.2, the types of domain walls are indicated by color-coded arrows around the frame of the image. In agreement with the results of Ref. [10,25], we observed 71°, 109° and 180° domain walls. It is noteworthy that 71° domain walls in this sample are of different nature than that of the ones observed in BFO thin films on STO substrates in chapter 2. As shown in the figure schematic (j), red-orange and light-dark blue pairs form 71° domain walls with tail-to-tail and head-to-head configurations, which is also named as charged domain walls, respectively. One should not be confused with the term ‘charged domain walls’ as they do not carry a net charge due to the required charge screening for reaching the thermodynamical equilibrium after the sample growth. Charge screening can be done by providing charge carriers from the other layers in the sample stack⁷ or creating vacancies in the vicinity of the domain wall. Unfortunately, it was not possible to determine the true conducting character of these charged domain walls due to the lack of an electrode layer.

One of the biggest challenges in the analysis of PFM measurements on these type of samples is the resolution that can be achieved. When the domain size is in the range of the tip radius,⁸ tip convolution effect might hamper the exact determination of the domain wall locations. Although accurate analysis of all present domain walls is not exactly possible with PFM, there are obvious examples that the sample under investigation contains charged 71° and neutral 109° domain walls. Report

⁷In this sample stack, there is no bottom or top electrode layer and the TSO substrate is known as a good insulator. Therefore it lowers the chances that there can be free charge carriers provided by the sample stack.

⁸In the acquisition of PFM images, ContDLC -diamond like carbon coated- probes were used from NanoAndMore GMBH that is specified with tip radius < 15 nm.

Figure 3.7: AFM and PFM analysis of a 60 nm thick BFO thin film on TSO (110)_o substrate. (a,e) are the topography images at different scan sizes, showing the puckered film surface. (b,f) are the out-of-plane and in-plane **amplitude** images, respectively. (c,g) are the out-of-plane and in-plane **phase** images, respectively. (d,h) are the zoomed-in images from (c,g) as indicated with the red squares. (i) is the concatenated image of (d and h), showing the present domains with color coding according to the representative unit cell structures in (j).

for the existence of charged domain walls in similar samples also corroborates our findings [25].

In brief, it was showed that the tilted pseudo-cubic structure of TSO (110)_o substrate results in selectivity for R₁ and R₂ structures among the possible four structural variants. This emphasizes that a distorted BFO unit cell structure is under the influence of substrate symmetry and it can be used for the manipulation of the domain wall types as will be further investigated in the next section. Additionally, the presence of 71°, 109° and 180° domain walls were observed.

BiFeO₃ on TbScO₃ (001)_o substrates

In the previous section, the distortion angle α is proposed as the reason for the selectivity among the structural variants. In order to facilitate this distortion angle as a symmetry breaking parameter even further, BFO thin film growth on TSO (001)_o substrate, where the α angle is in the substrate surface plane with isotropic in-plane lattice constants, was studied.

We will first focus on the structural analysis of 60 nm thick BFO thin film grown on SrO terminated⁹ TSO (001)_o substrates in order to identify the structural variants in the film. Figure 3.5 (3a-3f) summarizes the XRD-RSM measurements of the BFO sample on SrO terminated-TSO (001)_o substrate. The results of the measurements in a step-by-step order:

- ◇ (3a) and (3b) are the maps for (400)_{pc}¹⁰ plane family of the substrate and the film (in orthorhombic indices (008)_o plane map for the substrate) where the diffraction plane is along the [110]_o crystal axis ([001]_{pc} when $\phi = 0^\circ$) and [1-10]_o crystal axis ([010]_{pc} when $\phi = 90^\circ$), respectively.
- (3a) and (3b) show that the surface plane of the BFO film is parallel to that of the substrate.
- ◇ (3c) and (3d) are the (301)_{pc} plane family maps. In orthorhombic indices, (3c) and (3d) are the (116)_o and (1-16)_o maps where the diffraction plane is along the [110]_o crystal axis ([001]_{pc} when $\phi = 0^\circ$) and [1-10]_o crystal axis ([010]_{pc} when $\phi = 90^\circ$), respectively.
- In the (3c) map, the split of the two peaks can arise from the R₁+R₃ and R₂+R₄ structural pairs, from higher to lower Q_{out-of-plane} values respectively.

⁹This allows a growth of BFO samples with larger domains and less defects. In the next section, the differences between BFO thin films grown on A- and B-site TSO (001)_o will be shown.

¹⁰Because the substrate crystal cut is rotated 90°, in the $(hkl)_{pc}$ notation, now h represents the out-of-plane component. In other words, (400)_{pc} plane maps probe the surface plane of the sample as similar to the (004)_{pc} plane in the case of Figure 3.5 (1a & 1b).

In the (3d) map, the R_3+R_4 and R_1+R_2 structural pairs can form the split of two peaks from higher to lower $Q_{\text{out-of-plane}}$ values respectively.

- Based on the $(301)_{\text{pc}}$ plane family maps ((3c) and (3d)), we cannot conclude if there is any preference in the structural variants.
- ◇ (3e) and (3f) are the $(311)_{\text{pc}}$ plane family maps. In orthorhombic indices, (3e) and (3f) are the $(206)_{\text{o}}$ and $(026)_{\text{o}}$ plane maps where the diffraction plane is along the $[020]_{\text{o}}$ (i.e. $[0-11]_{\text{pc}}$ when $\phi = 45^\circ$) and $[200]_{\text{o}}$ (i.e. $[011]_{\text{pc}}$ when $\phi = 135^\circ$) directions, respectively.
- In the (3e) map, $(311)_{\text{pc}}$ planes of R_1 and R_4 structural variants give rise to the split of two peaks at different $Q_{\text{out-of-plane}}$ locations while sharing the same $Q_{\text{in-plane}}$ location.
- In the (3e) map, if existed, R_2 and R_3 structural variants would appear at the same location because they are both symmetric with respect to the incident X-ray beam direction. Their peak location would be at a $Q_{\text{out-of-plane}}$ value that is nearly the average value of the $Q_{\text{out-of-plane}}$ values for R_1 and R_4 with a slight difference in the $Q_{\text{in-plane}}$ value.
- In the (3f) map, R_1 and R_4 structural variants are symmetric with respect to the X-ray beam and they appear at the same position. If existed, R_2 and R_3 structural variants would appear at the locations of R_1 and R_4 variants in the (3e) map.
- ◇ From $(311)_{\text{pc}}$ maps, we conclude that BFO thin film on TSO $(001)_{\text{o}}$ substrate contain only R_1 and R_4 structural variants while R_2 and R_3 are missing.

Exact calculations of the crystal parameters for the TSO $(001)_{\text{o}}$ substrate and the BFO thin film are reported in the Table 3.1. It is noteworthy to mention that the α angle is estimated as 92.65° for the substrate while as 91.56° for the R_1 and R_4 BFO structural variants. This puts forth that the substrate α angle is the symmetry breaking parameter for the BFO growth by preventing the stabilization of R_2 and R_3 variants in the BFO thin film. To our knowledge, this is the first time reported that the angle in the substrate surface plane is used as symmetry breaking parameter in the growth of BFO thin films.

With the RSM measurement analyses, it is established that only two structural variants, namely R_1 and R_4 , are present in this film. This makes a detailed analysis of the domains and domain walls possible by PFM. Figure 3.8 shows the AFM topography (a) and PFM domains (b,c & e,f) of a 60 nm thick BFO film grown on SrO terminated TSO $(001)_{\text{o}}$. A flat film surface with unit cell height variations is observed in the topography image. Out-of-plane amplitude (b) and phase (c) PFM

Figure 3.8: AFM and PFM analysis of a 60 nm thick BFO thin film on TSO (001)_o substrate. (a) is the topography image. (b,e) are the out-of-plane and in-plane **amplitude** images, respectively. (c,f) are the out-of-plane and in-plane **phase** images, respectively. BFO thin film is uniformly 'down' oriented in the out-of-plane direction. In-plane polarization directions in the domains are indicated with red and black arrows in (f) according to the color coding in (d) where also the domain wall character is defined based on the relative directions of the polarization vectors (i.e. head-to-head etc.). Crystal axes are shown at the lower left corner of (e and f) for pseudocubic and orthorhombic indices, respectively. The lateral scale bar shown in (c) is valid for all AFM and PFM images.

images reveal a uniform domain structure in the film with very low noise signal level.¹¹ From the polarization switching experiments,¹² it is determined that the film is uniformly down oriented in the out-of-plane direction. In-plane amplitude (e) and phase (f) images represent the domain structure of the film. Although the determination of the absolute in-plane polarization direction is not possible with PFM, each direction is assigned a certain color by exploiting the fact that there are only R_1 and R_4 structural variants present in the film, as found out by the XRD analysis. Color coded correspondence of the structural variants forming the in-plane images are represented in Figure 3.8(d). For R_1 structural variant, the polarization vector is assumed along the $[-1-11]_{pc}$ direction, noting that in (hkl) notation, h is the out-of-plane component as shown in the inset of (e). For R_4 structural variant, the polarization vector is assumed along the $[-11-1]_{pc}$. Because the polarization vector changes in two Cartesian components between the adjacent domains of R_1 and R_4 variants, their interface is a 109° domain wall.

An interesting fact about the as-grown 109° domain walls in BFO thin films on TSO $(001)_o$ substrates is that they form between the R_1 and R_4 variants as opposed to the ones between R_1 and R_2 variants in the BFO thin films on TSO $(110)_o$ substrates, as shown in Figure 3.8. This new combination of structural variants theoretically requires the formation of domain walls with charged head-to-head and tail-to-tail polarization vectors within the adjacent domains as schematically depicted in Figure 3.8(d) with some examples indicated in (f). Additionally, in some regions parallel alignment of the polarization vectors with respect to the domain wall plane is expected due to the meandering nature of the domain walls. On the other hand, PFM technique is not suited to prove unequivocally the existence of charged domain walls as it cannot reveal with atomic resolution the polarization change in the vicinity of the domain walls.

In ferroelectrics, 180° domain walls have been long believed to be predominantly Ising type based on the Ginzburg-Landau-Devonshire (GLD) theory [32] where the polarization at the domain wall is supposed to disappear. However recent theoretical calculations [32,33] proposed that 180° domain walls can have a Bloch and Néel like components. In other words, the polarization vector might have a rotation component either along a plane parallel to the domain wall plane (in case of Bloch wall) or perpendicular to the domain wall plane (in case of Néel wall). Direct experimental evidence of the Bloch and Néel character of the ferroelectric domain walls has not been achieved yet although advances in transmission electron microscopy in the last decade helped to unravel some of the mystery. Jia et al. [34] reported the continuous rotation of the dipoles, closing the 180° flux of the polarization in tetragonal PZT thin films near the film-substrate interface. More recently, a periodic array of

¹¹It resembles the in-plane images, thus, likely that it is due to the buckling of the cantilever [31].

¹²Data not shown here as it will be discussed later.

flux-closure quadrants in 180° domain walls of PTO thin films was also reported by Tang et al. [35] where the film thickness determines the periodicity. For rhombohedral BFO structures, more complicated reconstructions were observed due to higher order structural variants as well as the richness of the domain wall types. Spontaneous formation of the vortex nanodomains [36, 37] and tetragonal-like charged nanodomains [25] were also reported in 109° domain walls of BFO thin films on TSO (110)_o and GdScO₃ (110)_o substrates.

A common feature of the flux-closure in the aforementioned studies is that they are observed in 109° domain walls with the polarization vector alternating in the out-of-plane direction. In BFO thin films on TSO (001)_o substrates, 109° domain walls occur between adjacent domains that are both down oriented. In this respect, the character of the domain walls is an interesting aspect whether they are purely Ising-like or combination of Bloch and Néel character with Ising type. A gradual structural transition between the R₁ and R₄ variants might take place either by shrinking of the pseudo-cubic unit cell structure to cubic symmetry (more Ising like behavior where the polarization is suppressed) or elongating along the out-of-plane direction of a tetragonal structure form with the polarization vector oriented down. The latter case would be different from Bloch and Néel like character as well. Therefore BFO thin films on TSO (001)_o might be a novel platform to study the changes in the ferroelectric dipoles in the vicinity of the domain walls.

In chapter 2, parameters influencing the BFO growth were discussed in detail. Substrate vicinality was also mentioned as a symmetry breaking parameter among the structural variants. The main idea is that the BFO structural variants tilting towards the step edge cannot be stabilized as they are hampered by the substrate [38]. Taking advantage of this factor as well as substrate symmetries with the α angle on the surface plane, a 60nm thick BFO thin film on a SrO terminated LSMO electrode layer (5 nm thick) on TSO (001)_o substrate with a miscut angle of $\sim 0.15^\circ$. This resulted in the growth of nearly single domain BFO thin films. Although there are regions that still contains the mixture of both R₁ and R₄ structural variants, in overall we managed to obtain a film with a preference for one structural variant predominantly. Figure 3.9 (a&e) shows the topography images of the sample at different scan sizes. AFM surface images indicate a BFO growth where the film is mimicking the substrate topography by maintaining the straight step edges with unit cell height variation. These measurements ensure that step edges are preserved throughout the film and their symmetry breaking effect is expected to emerge in this film. Figure 3.9 (b,c) are the out-of-plane phase and in-plane phase images respectively. Their concatenated image (d) shows that the film is nearly single phase. A square area of the sample is poled with -6V_{tip} bias in order to switch the polarization direction out-of-plane, revealing that the as-grown sample is ‘down’ oriented.

(f,g) are the out-of-plane and in-plane phase images after poling respectively. The concatenated image in (h) reveals all the domains with a color coded polarization vectors as depicted in (i) after poling. It is noteworthy to mention that poling results in formation of mostly 180° domain walls between the light-blue and red domains where there is no structural change when the polarization is rotated 180° within the same structural variant. However some regions, shown in yellow in (h), underwent a structural transition resulting in the formation of 71° and 109° domain walls between the light blue-yellow and red-yellow domain pairs respectively. Even though we were not able to find out the actual reasons what drives the occurrence of the structural transitions in some parts and not in the rest, more investigation on such samples might provide useful information regarding the understanding of the polarization switching in BFO samples. Upon achieving a detailed understanding of polarization switching, artificial domains and domain walls can be created by PFM, thus, controlled charged domain walls and vortex-like configurations can be obtained. In this respect, one further interesting study could be that applying the tip DC bias only in one direction in the fast scan axis of the PFM microscope. In the standard settings of the Omicron and Bruker Dimension Icon microscopes, DC bias is applied both in trace and retrace directions of the fast scan axis. A modification in the software is required to enable the option to apply the DC bias only either in the trace or retrace direction. In this way, a correlation might be found out between the tip scan axis and the changes in the in-plane polarization direction of the sample as done for R-like BFO thin films on STO [39] and for coexisting T-like and R-like phase of BFO thin films on LAO substrates [40].

In this section, it was show that the surface angle α on TSO $(001)_o$ orthorhombic substrates can be used as a symmetry breaking parameter. Selectivity was achieved for R_1 - R_4 structural variant pair over among the four possible variants, resulting in the formation of as-grown meandering 109° domain walls. BFO thin films on TSO $(001)_o$ opens a novel platform to investigate the Ising-like nature of the charged domain walls and their electrical properties as well as for the polarization switching phenomena in BFO thin films.

3.3.2 Influence of growth kinetics over BiFeO_3 growth on orthorhombic substrates

In chapter 2 it was shown that growth dynamics, controlled by the surface termination, plays a crucial role in the growth of BFO thin films on STO substrates. In this section, it is aimed to test the generality of this result by investigating the growth on TSO substrates. Here, we investigated the role of the terminating layer of the TSO $(110)_o$ and TSO $(001)_o$ substrates on the growth of BFO thin films.

First the structural comparison of 60 nm thick BFO thin films grown on ScO_2 (B-

Figure 3.9: AFM and PFM analysis of a 60 nm thick BFO thin film on SrO / LSMO (5nm) / TSO (001)_o substrate upon polarization switching experiment. (a,e) are the topography images at different scan sizes, featuring the step-edge preservation on the film surface. (b,c,d) are the out-of-plane, in-plane **phase** images and their concatenated image before poling, respectively. (f,g,h) are the out-of-plane, in-plane and their concatenated **phase** image after poling the central $5 \times 5 \mu\text{m}^2$ area with $-6V_{\text{tip}}$ bias, respectively. (i) shows the schematics for 4 variants (R_1 and R_2 structural variants, each with polarization either ‘up’ or ‘down’ oriented). Also a color coding definition is given for different domain walls that can be found in the concatenated images (d and h). The lateral scale bar shown in (a) is valid for all the other images except (e).

site) terminated and SrO (A-site) terminated TSO (110)_o substrates are provided. RSM measurement results for BFO thin films are given in Figure 3.5 (1(a-f) and 2(a-f)) on B-site and A-site TSO (110)_o substrates respectively. Detailed analysis of the RSM measurements for BFO on B-site TSO (110)_o is done on page 36. The step-by-step analysis of the RSM measurements for BFO thin films on A-site TSO (110)_o, see Figure 3.5 (2a-2f), is as following:

- ◇ (2a) and (2b) are the (004)_{pc} (in orthorhombic indices (440)_o) plane maps where the diffraction plane is aligned along the $[1-10]_o$ ($[010]_{pc}$ when $\phi = 0^\circ$) and $[001]_o$ ($[100]_{pc}$ when $\phi = 90^\circ$) crystal directions respectively.
- (2a) and (2b) show that the BFO film is strained to the substrate and the surface plane of the film is parallel to that of the substrate, irrespective of the alignment of the diffraction plane with respect to the crystal axis.
- ◇ (2c) and (2d) are the (103)_{pc} plane family maps. In orthorhombic indices (420)_o and (33-2)_o maps where the incident X-ray beam is aligned along the $[1-10]_o$ ($[010]_{pc}$ when $\phi = 0^\circ$) and $[001]_o$ ($[100]_{pc}$ when $\phi = 90^\circ$) crystal directions respectively.
- In (2c) map, the split two peaks can arise from the R_1+R_3 and R_2+R_4 structural pairs, from higher to lower $Q_{\text{out-of-plane}}$ values respectively. In the (2d)

map, R_3+R_4 and R_1+R_2 structural pairs can form the split peaks from higher to lower $Q_{\text{out-of-plane}}$ values respectively.

- Based on the $(103)_{\text{pc}}$ plane family maps ((2c) and (2d)), we cannot conclude if there is any preference in the structural variants.
- ◇ (2e) and (2f) are the maps for $(113)_{\text{pc}}$ plane family, in orthorhombic indices $(422)_{\text{o}}$ and $(242)_{\text{o}}$ when incident X-ray beam is along $[1-11]_{\text{o}}$ ($[110]_{\text{pc}}$ when $\phi = 45^\circ$) and $[-111]_{\text{o}}$ ($[1-10]_{\text{pc}}$ when $\phi = 135^\circ$) crystal directions, respectively.
- In the (2e) map, $(113)_{\text{pc}}$ planes of R_1 and R_4 structural variants give rise to split peaks at different $Q_{\text{out-of-plane}}$ locations while sharing the same $Q_{\text{in-plane}}$ location. R_2 and R_3 structural variants appear at the same location because they are both symmetric with respect to the incident X-ray beam direction. Their peak location is at a $Q_{\text{out-of-plane}}$ value that is nearly the average value of the $Q_{\text{out-of-plane}}$ values for R_1 and R_4 with a slight difference in the $Q_{\text{in-plane}}$ value with respect to them.
- In the (2f) map, R_1 and R_4 structural variants are symmetric with respect to the X-ray beam and they appear at the same position. R_2 and R_3 structural variants appear at the locations of R_1 and R_4 variants in the (2e) map.
- ◇ From (2a-2f) RSM measurements, we conclude that all the structural variants do exist in the BFO thin film on A-site TSO $(110)_{\text{o}}$ substrate. Intensity difference in some of the peak gives a clue for uneven distribution of the existing structures though quantifying is not easy.

Comparing the RSM measurements of the BFO thin films on B-site and A-site TSO $(110)_{\text{o}}$, structural differences between the samples are found. BFO on B-site TSO $(110)_{\text{o}}$ substrate only has two structural variants with tilted $(001)_{\text{pc}}$ surface planes with respect to that of the substrate whereas BFO on A-site TSO $(110)_{\text{o}}$ contains all the structural variants with parallel surface planes to the substrate. Crystal structure parameters such as lattice constants and tilt angles can be seen in the Table 3.1. It is worth to mention that symmetry breaking effect of the α angle on the B-site TSO is not observed on A-site TSO due to the existence of structural variants that are tilted in either clockwise and anti-clockwise directions. This implies that in case of half-cut octahedra (B-site termination), α angle effect is transferred to the film whereas complete octahedra (A-site termination) promotes the stabilization of BFO structure in any tilting direction. This finding to some extent contradicts with the results of Chen et al. [27] where they claimed that 10 unit cells of STO buffer layer is needed to decouple the octahedral connection between the DSO substrate and BFO thin film. In our experiments, we observed that single SrO layer is sufficient

to change the crystal stabilization of the BFO structural variants as well as to reduce the effect of the substrate symmetry.

AFM analysis of the surface of a 60 nm thick BFO film on a B-site TSO (110)_o substrate shows needle-like sharp topographic features (also referred as puckered surface), see Figure 3.10(a). The corresponding domain morphology exhibits only two structural variants with as grown 109° domain walls, see the PFM image in Figure 3.10(b), which are dominantly pinned by the topographic features. On the other hand, the surface of a 60 nm thick BFO film on a A-site TSO (110)_o substrate shows atomically flat terraces separated by unit cell height steps (Figure 3.10(c)) similar to the initial surface of the substrate. Detailed PFM analysis indicates that 71° domain walls are present (Figure 3.10(d)). In Figure 3.10(b,d) 109° and 71° domain walls are indicated in red and blue at the right bottom corner of the images respectively. The difference between domain size/width in these films is about one order of magnitude. BFO thin film on B-site TSO (110)_o substrate exhibits a domain width of about 20-30 nm, whereas BFO thin film on A-site TSO (110)_o substrate exhibit a domain width in the order of 200-300 nm. This reveals that BFO growth on B-site TSO (110)_o substrate has a higher nucleation density caused by a lower mobility of the arrived species on the substrate surface so that domain walls are pinned by the topographic features, forming much smaller domains as compared to BFO grown on A-site TSO (110)_o.

In light of these results, we conclude that selectivity between the as grown 71° and 109° domain walls in BFO thin films on TSO (110)_o substrates is achieved by interface engineering, where the key determining factor is not related to the screening charges i.e. depolarization field, as previously believed [10], but to the growth dynamics at the initial stages of growth.

Effect of the SrO termination layer on TSO (001)_o is also investigated. 60 nm thick BFO thin films were grown on B-site and A-site TSO (001)_o substrates. Figure 3.11 summarizes the AFM and PFM measurements on these samples where the images in the upper row are for BFO on B-site TSO (001)_o and lower row for BFO on A-site TSO (001)_o. (a,d) are the topography images with some trenches visible in (a) in contrary to the flat film surface in (d). This already indicates that SrO termination promotes more uniform and defect free growth of BFO thin films on TSO (001)_o substrates as well. (b,e) are the in-plane amplitude and (c,f) are the in-plane phase images. Out-of-plane images are not shown as they are uniformly poled in ‘down’ direction. PFM images point out that the domain size varies between the films in favor of enlarged domains for the BFO thin films on A-site TSO (001)_o. In order to quantify this, domain walls are labeled with red in the amplitude images and the area occupied by them is normalized with respect to the total image area. This reveals that the ratio of the domain walls is 21 (±3)% and 8 (±1)% in BFO

Figure 3.10: (a,c) Topography and (b,d) PFM in-plane phase images of 60 nm thick BFO thin films grown on B-site and A-site TSO (110)_o substrates respectively. In the lower right corners of (b and d), 109° and 71° domain walls are indicated in red and blue in the same order to guide the reader for the domain width with the help of scale bars as shown.

Figure 3.11: (a,d) Topography, (b,e) PFM in-plane **amplitude** and (c,f) PFM in-plane **phase** images of 60 nm thick BFO thin films grown on B-site and A-site TSO (001)_o substrates respectively. (a,d) topography image comparison shows that BFO thin film on B-site TSO (001)_o has more defective trenches than BFO on A-site TSO (001)_o. In (b,e) amplitude images, domain walls are labeled in red. Amplitude and phase image comparisons between the samples indicates that BFO thin film on B-site TSO (001)_o has smaller domains in general, pointing out to a difference in the growth kinetics. The lateral scale bar shown in (f) is valid for all the images except (a,d).

thin films on B-site and A-site TSO (001)_o substrates respectively.

The results presented in Figure 3.10 and Figure 3.11 strengthen our hypothesis that the nucleation density and mobility of the species vary depending on the termination of the substrate surface. A-site terminated surfaces enhance the surface diffusivity, which dramatically reduces the surface roughness of the grown BFO films.

3.4 Conclusion

This chapter investigated the BFO thin film growth on orthorhombic TSO (110)_o and TSO (001)_o substrates with regards to the substrate symmetry and growth kinetics. The main findings of this study can be summarized as following:

- On B-site terminated TSO (110)_o substrate, BFO thin film is consisted of R₁ and R₂ structural variants in a stripe-like shape with narrow domain widths. The selectivity for R₁-R₂ pair is created due to the fact that α angle lying in (010)_{pc} plane is an obtuse angle and this exerts a force on BFO structural variants to have a tilt in the same direction through the help of half octahedra on B-site surface. Additionally, narrow domain width indicates a low surface diffusivity. This might be related to the surface being terminated with half octahedra that requires formation of higher number of bonds during growth.
- On A- and B-site terminated TSO (001)_o substrate, BFO thin film is consisted of R₁ and R₄ structural variants with meandering head-to-head, tail-to-tail and parallel 109° domain walls. An obtuse α angle lies in the (001)_{pc} surface plane and this promotes the stabilization of structural variants that share the distortion angle in the same direction as the substrate. This is a novel example of how substrate symmetry can be used to stabilize a new pair of structural variants in BFO thin films.
- On A-site terminated TSO (110)_o substrate, BFO thin film do exhibit all types of structural variants with wider domain sizes compared to the film on B-site TSO (110)_o substrate. This indicates that higher surface diffusivity for BFO species can be achieved on A-site terminated TSO surfaces.
- Comparison of average domain size in BFO thin films on A- and B-site terminated TSO (001)_o substrates also supports the hypothesis that A- site terminated surfaces enables a higher surface diffusivity of BFO species.

In this chapter it is showed that the substrate symmetry and growth kinetics can be used to manipulate the growth of BFO thin films on TSO (110)_o and TSO (001)_o substrates with a careful choice of surface termination. It is worth to emphasize that results on A- and B- site TSO (110)_o substrates reveals that growth kinetics

is a determining factor for selectivity between 71° and 109° domain walls instead of screening charges. More interestingly, for the first time to our knowledge, substrate symmetry is reported to result in stabilization of R_1 - R_4 structural pair in BFO thin films on TSO (001)_o substrates. This type of samples provides a novel platform to study the domain wall types in ferroelectrics regarding Ising, Bloch and Néel like behavior.

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Chapter 4

Interface effects on conduction in BiFeO₃ thin film stacks

Abstract: Leakage currents in BiFeO₃ thin films can be detrimental to its properties. Hence, there have been significant efforts to understand the governing mechanisms of conductivity in BiFeO₃ thin films as well as to find ways to reduce it. Due to the variations in the crystal structure and growth conditions of BiFeO₃ thin films, various bulk and interface limited conduction mechanisms were reported in literature. In this chapter, these conduction mechanisms were investigated in order to understand the nature of leakage currents in BiFeO₃ thin film stacks. In particular, the influence of electrode layers and the surface termination of the substrates were studied to control the leakage current. La_{2/3}Sr_{1/3}MnO₃ thin films and Nb:SrTiO₃ substrates were selected as electrode layers due to (i) their different work functions so that it can potentially give rise to a different Schottky barrier at the BiFeO₃-electrode interface and (i) both can provide A- and B-site surface termination unlike SrRuO₃ thin films that tend to only terminate with a SrO atomic plane. In this study, it is found that the main conduction mechanism is interface limited Schottky emission in BiFeO₃ thin films. It was shown that the use of Nb:SrTiO₃ substrates as an electrode can dramatically reduce the leakage current as compared to La_{2/3}Sr_{1/3}MnO₃ electrode layers because of the higher Schottky barrier at the BiFeO₃-Nb:SrTiO₃ interface. Additionally, the effects of the surface termination of the electrode layers on the leakage current were studied. This has revealed that the addition of a single SrO layer lowers the Schottky barrier height at the BiFeO₃-La_{2/3}Sr_{1/3}MnO₃ interface by modifying the work function of the electrode. In contrast, SrO layer surface termination leads to a higher Schottky barrier height at the BiFeO₃-Nb:SrTiO₃ interface by improving the BiFeO₃ thin film growth quality.

4.1 Introduction

Understanding the conduction mechanisms in metal-ferroelectric-metal (MFM) structures is very crucial as it governs the properties of devices such as ferroelectric memory devices, ferroelectric field-effect transistors and ferroelectric tunnel junctions. Although, a vast literature exists on this topic, featuring mostly BaTiO₃ (BTO), lead-zirconate-titanate (PZT) and BiFeO₃ (BFO) materials systems, the exact nature of the conduction mechanisms and leakage currents is still subject of debate. The complications arise due to the semiconductor nature of the ferroelectric materials where the conduction can be modulated by the intrinsic electrical polarization and by the presence of defects which can create trap states in ceramic materials. Conduction mechanisms in ferroelectric and dielectric materials can be classified into two categories, namely interface limited and bulk limited conduction. Among the interface limited conduction mechanisms, Schottky emission, Fowler-Nordheim tunneling, direct tunneling and thermionic-field emission can be listed where the main governing factor is the interface created between the metal and the ferroelectric material. On the other hand, for the bulk-limited conduction mechanisms, Poole-Frenkel emission, ohmic conduction, space charge limited conduction, ionic conduction, grain-boundary limited conduction and hopping conduction can be mentioned [1]. For example, Schottky emission was found to be the dominating conduction mechanism in PZT [2–5] and BFO [6–9] thin films. Additionally, space charge limited conduction was reported in PZT [10] and in BFO [8, 9, 11, 12] thin films. It is important to mention that there is no consensus over the conduction mechanism in ferroelectric materials in the literature. The widespread contradicting reports can be due to the fact that in MFM structures, typically various conducting processes are present at the same time and contribute to the leakage current. One mechanism might be more dominant than others depending on the measurement circumstances i.e. temperature, voltage regime, choice of electrode materials and differences due to structural variations between thin films in different studies. Moreover these conduction mechanisms are not linearly additive; rather, they result in nonlinear integral equations for the total leakage current [13]. This also complicates the analysis of the I - V characteristics of an MFM structure. Therefore electrical analysis of MFM structures requires the understanding of all these processes and their contribution to the overall characteristic of the samples.

When discussing the electrical properties of the ferroelectric materials, it is important to mention that they are generally treated as wide band gap semiconductors [3, 14]. Most of the titanate based ferroelectrics are shown to be p -type in bulk due to the impurities with lower valences compared to the ions that they substitute for [15–17]. On the other hand, oxygen vacancies in such ferroelectric thin films result in n -type character due to the electrons left behind in the system. In the

particular case of BFO, its conduction properties are not known accurately and it is treated either as *p*-type due to the Bi deficiencies [18] or as *n*-type due to oxygen vacancies [19, 20] by different research groups. In this study, the results of current vs voltage (IV) measurements were interpreted with the assumption of BFO being either *n* or *p*-type. As discussed in this chapter, it is claimed that BFO samples in this study act as *n*-type semiconductors.

In this section, first, the basics of the relevant electronic conduction mechanisms for the ferroelectric materials are described. Subsequently a brief summary of various reports in literature for electrical properties of BTO, PZT and BFO ceramics is given which is followed by the motivation of this chapter.

4.1.1 Interface Limited Conduction Mechanisms

For the interface limited conduction mechanisms, the nature of the leakage current is determined by the electrical properties at the ferroelectric-metal interface. The most important parameter in such mechanisms is the barrier height between the ferroelectric and metal layers where it determines the thermionic emission as well as the tunneling current. In Schottky emission, also known as thermionic emission, the current is highly dependent on temperature, whereas tunneling based conduction mechanisms are insensitive to the changes in temperature. Next to the barrier height and temperature, the effective mass of the conduction carriers is also very crucial in the interface-limited mechanisms.

In general, ferroelectrics (i.e. wide band gap semiconductors) are good insulators and do carry small number of free carriers in their conduction band. When an *n*-type semiconductor is brought into contact with a metal, charge transfer takes place between the metal and the semiconductor layers. If the semiconductor electron affinity (χ) is greater than the metal work function (ϕ_m) (i.e. $\phi_m < \chi$), an ohmic contact forms. In contrast, if the metal work function is larger than the semiconductor electron affinity, a potential barrier (ϕ_B) forms at the interface, the so called Schottky barrier. The Schottky barrier height between an intrinsically pure ferroelectric and a metal is given by:

$$\phi_B = \phi_m - \chi. \quad (4.1)$$

This equation was developed by Schottky and Mott (1938) [21, 22] and involves some assumptions, namely; (i) no changes occur in the surface dipole contributions to ϕ_m and χ when the metal-semiconductor interface is created; (ii) there are no localized interface states. This is the so called Schottky-Mott limit and is schematically described in Figure 4.1(a) for an interface between a metal and an *n*-type semiconductor. In this situation, electrons that travel from the semiconductor to the metal leave positive charges behind, causing an upward band bending (i.e. a

Figure 4.1: Representation of the Schottky barrier formation at a metal- n -type semiconductor interface. (a) The Schottky-Mott limit is shown. (b) The case lying in between Schottky-Mott and Bardeen limits where an interfacial layer forms between the metal and the semiconductor. The notations are described as following: ϕ_m is the metal work function, ϕ_B is the Schottky barrier height, ϕ_0 is the neutral level (above E_V) of interface states, Δ is the potential across interfacial layer, χ is the electron affinity of semiconductor, ψ_{bi} is the built-in potential, δ_{eff} is the effective thickness of interfacial layer, Q_{sc} is the space-charge density in semiconductor, Q_{ss} is the interface trap charge, Q_M is the surface-charge density on metal, D_{it} is the interface trap density. Adapted from Ref. [24].

depletion region forms in the vicinity of the interface). However, this equation is too simple to explain all the experimental results. Therefore Bardeen (1947) [23] defined the other extreme situation where the barrier height is independent of the metal work function and proposed that the Fermi level of the semiconductor can be pinned by the surface states that are created in the semiconductor band gap by the metal.

Schottky-Mott [21, 22] and Bardeen [23] defined the conditions for ideal metal - semiconductor junctions in two extremes. However in reality most of the junctions lie somewhere between the Schottky-Mott and Bardeen limits as depicted in Figure 4.1(b). This is quantitatively defined as $S = d\phi_b/d\phi_m$ with $S = 1$ and $S = 0$ being the Schottky-Mott and Bardeen limits, respectively. The value of S depends on the nature of the semiconductor and there have been studies that tried to correlate it with the ionic and covalent nature of the semiconductor [25] as well as with its dielectric constant [26, 27]. Unfortunately, the formulations developed in these studies do not always agree with the experimental findings [28]. For ferroelectric oxides S is claimed to be around 0.5 [13].¹ It is important to emphasize that the Schottky barrier does not solely depend on the difference between the metal work function and the semiconductor electron affinity. The surface states created in the semiconductor band gap due to the metal layer, external dopants, dangling bonds on the surface and

¹For more details, the reader is referred to [28].

discontinuity at the interface etc. play a role in the determination of the Schottky barrier as well.

In conventional semiconductors, the n -type or p -type character of the material, depending on the dopant characteristics, determines the main charge carriers. In that case the Schottky barrier at the metal-semiconductor interface plays a role in the overall conduction of the system. Unlike the conventional semiconductors, in the case of oxide ferroelectrics on elemental metal electrodes the barrier height for holes is much higher than the barrier height for the electrons as was shown by Robertson and Chen [29]. Therefore, in oxide ferroelectrics the main injected charge carriers are electrons, thus the leakage current is an electron current and not a hole current.

Schottky Emission

Thermionic emission is a process where the thermally induced activation energy is responsible for inducing the flow of charge carriers over a potential barrier. This can be realized when the thermal energy is higher than the work function of the material. Charge carriers might be electrons, holes or ions. The classical example of the thermionic emission is the emission of electrons from a hot cathode into the vacuum in a vacuum tube at high temperatures (around 1000K). In electronic devices, this phenomenon is usually referred as Schottky emission for conduction between metal and semiconductor layers. If the carriers in the metal layer have enough thermal energy to overcome the Schottky barrier, they can enter to semiconductor layer. Hence, this process is highly temperature dependent. The general expression for the Richardson-Schottky emission is given as [1]:

$$J = A^* T^2 \exp \left[\frac{-q(\phi_B - \sqrt{qE/4\pi\epsilon_r\epsilon_0})}{kT} \right] \quad (4.2)$$

with

$$A^* = \frac{4\pi q k^2 m^*}{h^3}$$

where J is the current density, A^* is the effective Richardson constant, m^* is the effective electron mass in the semiconductor, T is the absolute temperature, q is the electronic charge, $q\phi_B$ is the Schottky barrier height, E is the electric field across the semiconductor, k is the Boltzmann's constant, h is the Planck's constant, ϵ_0 is the permittivity in vacuum, and ϵ_r is the optical dielectric constant of the semiconductor (i.e. the dynamic dielectric constant). It is noteworthy to mention that the exponential term in this formula represents the charge injection at the metal-semiconductor interface. Additionally, the optical dielectric constant should be used over the static dielectric constant due to the following reason. If the electron transit time from the metal-semiconductor interface to the maximum barrier height

position is smaller than the dielectric relaxation time of the semiconductor, the dielectric material does not have enough time to be polarized during the emission process. Therefore, only the high frequency processes can contribute in response to the emission process and the optical dielectric constant is the relevant parameter to be taken into account.

The Richardson-Schottky model was later on modified by Simmons [30] for solids in which the electron mean free path is smaller than the film thickness. In that case, charge injection is controlled by the barrier at the metal-semiconductor interface; while the charge carriers pass through the bulk of the film. They are scattered several times and all the defects and the trap states can influence the charge transport. Taking such drift diffusion factors into account, Simmons proposed the following modification to the Richardson-Schottky emission formula:

$$J = 2q \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \mu E \exp \left[\frac{-q(\phi_B - \sqrt{qE/4\pi\epsilon_r\epsilon_0})}{kT} \right] \quad (4.3)$$

where μ is the carrier mobility in the semiconductor and the rest of the notation as defined before. While the exponential term describes the charge injection processes at the interface, the pre-exponential term is now modified to contain the carrier mobility and the voltage dependence during the charge transport through the bulk of the film.

Graphical representation of the Simmons-Richardson-Schottky (SRS) equation (Eqn. 4.3) can be done in two ways, namely for constant temperature or constant voltage. For constant temperature, $T \ln(I/T^{3/2}V)$ vs $V^{1/2}$ should give a straight line for all temperatures. Firstly, this representation is used to verify that the conduction mechanism is the Schottky emission, if all the measurements at different temperatures overlap. Secondly, from the slope of the linear part, the optical dielectric constant can be extracted and compared to the values that are obtained from independent measurements. Constant voltage representation of the Schottky emission equation is used to extract the Schottky barrier height from the IV measurements. This can be done according to the well-defined procedure by Pintilie [3]. Equation 4.3 can be expressed as following for the constant voltage representation:

$$\ln \left(\frac{J}{T^{3/2}} \right) = \ln \left(2q \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \mu E \right) - \left[\frac{q(\phi_B - \sqrt{qE/4\pi\epsilon_r\epsilon_0})}{kT} \right] \quad (4.4)$$

In Eqn. 4.4, the first term on the right hand side is constant while the second term is proportional to the apparent potential barrier where ϕ_{app} is defined as $\phi_{app} = \phi_B - \sqrt{qE/4\pi\epsilon_r\epsilon_0}$. In the graphical representation for constant voltage axis, $\ln(J/T^{3/2})$ vs. $1/T$ gives a straight line while the slope gives ϕ_{app} and the intercept value is

proportional to μE . Based on these calculations, $\phi_{app} - V^{1/2}$ can be plotted and ϕ_B can be extracted from the intercept at $V = 0V$. In the remainder of this chapter, this procedure is applied to calculate the Schottky barrier height.

Fowler-Nordheim Tunneling

When electrons face a barrier that requires a higher energy than they possess to overcome the barrier, they are reflected back according to classic mechanics. However, quantum mechanics permits a special phenomenon, known as tunneling, by which an electron wave function can penetrate through the potential barrier when the barrier is thin enough. Therefore, the probability of electrons existing on the other side of the barrier is not zero because of the tunneling effect.

In relation to the conduction in oxide semiconductors, two mechanisms can be described based on tunneling. The first one is direct tunneling, provided that the semiconductor barrier layer is thin enough so that direct tunneling can take place through the entire thickness of the film. This mechanism is mostly relevant for ultra-thin oxide ferroelectrics when they are exploited in memristor devices as ferroelectric tunnel junctions. The second conduction mechanism that is based on the tunneling phenomenon, is the Fowler-Nordheim (F-N) tunneling. The main difference with the direct tunneling is that the tunneling takes place at the metal-semiconductor interface through the barrier width instead of the entire thickness of the film. F-N tunneling occurs when the applied field is large enough (i.e. usually at high voltages) so that the electrons can tunnel through the barrier and enter the semiconductor layer. The general expression for F-N tunneling is given as below [1]:

$$J = \frac{q^3 E^2}{8\pi h q \phi_B} \exp \left[\frac{-8\pi(2m_T^*)^{1/2}}{3h q} \frac{\phi_b^{3/2}}{E} \right] \quad (4.5)$$

where m_T^* is the tunneling effective mass in the semiconductor and the rest of the notations is the same as defined before. As seen in Eqn. 4.5, F-N tunneling current depends on the barrier height, while it is independent of the temperature. The latter is the most distinctive feature of the F-N conduction mechanism. This type of conduction is usually observed at low temperatures when the Schottky emission is suppressed and the tunneling current is dominant. In order to determine whether the conduction mechanism of a metal-semiconductor junction is F-N tunneling, a plot of $\ln(J/E^2)$ vs. $1/E$ for several temperatures can be used. This plot should give a straight line without temperature dependence.

4.1.2 Bulk Limited Conduction Mechanisms

Other than the limiting factors set by the metal-semiconductor interface, electrical properties of the oxide ferroelectrics can be a bottleneck for the overall conduction in such systems. These are usually referred to as bulk limited conduction mechanisms. The common denominator lies in the trap energy levels in the semiconductor that determine the overall electrical characteristic of the system. The bulk limited conduction in semiconductor materials include the following mechanisms: Ohmic conduction, Poole-Frenkel (P-F) emission, space charge limited conduction, ionic conduction, grain-boundary limited conduction and hopping conduction. Among these possible mechanisms, only the most relevant mechanisms in oxide ferroelectric will be described in this section.

Ohmic Conduction

Ohmic conduction refers to the movement of mobile charge carriers, namely the electrons in the conduction band and the holes in the valance band under an applied electric field. In this case, a linear relationship between the applied electric field and the current density exists. Although ohmic conduction is typically found in materials without a band gap, i.e. metals and in some semiconductors with low energy band gap, i.e. high quality Si, there will still be a small number of carriers available in wide band gap semiconductors, including oxide ferroelectrics. It can either be provided by thermal excitation of electrons to the conduction band from the valance band or by the impurity levels in the band. The carrier density will be very small due to the large band gap of the oxide semiconductors, however, it will not be zero. For example, in the resistive switching behavior in dielectric semiconductors, ohmic conduction is the dominant mechanism in the low resistance state [31]. The general expression for the ohmic conduction is given below [1]:

$$J = \sigma \frac{V}{d} = nq\mu \frac{V}{d}, \quad n = N_C \exp\left[\frac{-(E_C - E_F)}{kT}\right] \quad (4.6)$$

where σ is electrical conductivity, V is the applied voltage, d is the film thickness, n is the number of electrons in the conduction band, μ is electron mobility, N_C is the effective density of states of the conduction band, E_C and E_F are the conduction and Fermi levels in the energy spectrum respectively. As can be seen in Eqn. 4.6, ohmic conduction depends linearly on the electric field due to the electrons in the conduction band or the holes in the valance band. This type of conduction is usually observed at low voltages in the current-voltage (I-V) characteristics of semiconductor films. However, in an alerting paper, Scott [32] drew attention to the similarity between the SRS equation (Eqn. 4.3) and the ohmic equation (Eqn. 4.6). At low voltages,

the exponential part of the SRS equation converges to unity and the overall current might seem to have a linear dependence on the electric field. Hence, SRS conduction may be misinterpreted as ohmic conduction. In order to determine the exact type of conduction, the thickness dependence (J vs. $1/d$) of the sample has to be studied.

Poole-Frenkel Emission

Poole-Frenkel emission refers to a conduction mechanism where the electrons can be thermally excited from the trap levels into the conduction band of the semiconductor. It is similar to the Schottky emission mechanism where the potential barrier has to be overcome by the thermal excitation of the charge carriers. Since the emission from a trap level into a conduction band might be anywhere in the bulk of the semiconductor film, P-F mechanism is sometimes referred to as the internal-Schottky mechanism as well. However, in the P-F mechanism the barrier that needs to be overcome by electrons is the potential difference between the trap center level and the conduction band level. Unlike the potential barrier that forms at the metal-semiconductor interface in the Schottky emission, trap centers can be distributed anywhere in the bulk of the semiconductor. An applied electric field can reduce the potential energy of electrons in trap centers so that their thermal energy can be high enough to excite them into the conduction band. Upon application of an electric field, electrons can travel in the conduction band for a brief amount of time until they are caught by another empty trapping center. Those electrons that can reach the metal layer create the P-F current. Assuming ohmic contacts on both sides of the semiconductor layer, P-F emission can be modeled as following [1]:

$$J = q\mu N_C E \exp \left[\frac{-q(\phi_T - \sqrt{qE/\pi\epsilon_r\epsilon_0})}{kT} \right] \quad (4.7)$$

where $q\phi_T$ is the trap energy level and the rest of the notations is the same as in Eqn. 4.2 and 4.6. According to P-F emission equation (4.7), constant temperature graphical representation, $T \ln(J/E)$ vs. $E^{1/2}$, should give a straight line. Therefore, in I-V measurement analysis, this plot will be used to fit the data for P-F emission. Additionally, the general dependence of the current on voltage for P-F and Schottky emissions is very similar. However, the main difference between the two mechanisms is that P-F emission assumes ohmic contact on both sides of the semiconductor layer whereas Schottky emission is controlled by the interface between the metal and the semiconductor. In other words, P-F emission is electrode independent on both positive and negative bias directions, which makes the current behavior symmetric. On the contrary a diode-like behavior can be obtained for Schottky emission in case of asymmetric interfaces (due to a possible use of different type of electrodes). Alternatively, extraction of the optical dielectric constant (ϵ_r) from the

constant temperature representations for P-F and Schottky emissions can be used for comparing the models to fit the theoretically expected values of ϵ_r .

Space-Charge-Limited Conduction

The space charge phenomenon usually refers to the accumulation of charges in a certain region of a dielectric medium (including semiconductors and vacuum). Traditionally, it is identified in vacuum tubes upon a thermionic emission from a metal source into the vacuum. When the conductivity of the dielectric medium is not high enough, accumulation of charges starts to occur in the dielectric medium. This phenomenon does not take place in metals since the electrons flow away from the medium due to higher conductivity.

Space-Charge-Limited conduction refers to a mechanism in semiconductors where at low voltages, the current shows a linear dependence (Ohmic regime) and upon a further voltage increase, with an abrupt change, quadratic dependence (V^2) starts to appear. In the latter regime, the current also has an inverse cubic dependence on the thickness (d^{-3}). At even higher voltages, the dependence goes into V^3 regime, again with an abrupt change. The thickness dependence also changes from d^{-3} to d^{-5} . A simplified version of the expression for the SCL conduction mechanism is given by Child's law:

$$J = \frac{9}{8} \mu \epsilon \frac{V^2}{d^3} \quad (4.8)$$

where ϵ is the static dielectric constant and the rest of the notation as defined in Eqn. 4.6. From Eqn. 4.8, it can be seen that $\ln(J)$ vs. $\ln(V)$ should give a straight line with a slope of 2. This plot can be used to identify a conduction mechanism being space charge limited. Further, thickness dependence is a valuable method to finally confirm that the conduction is space-charge-limited as d^{-3} and d^{-5} dependence is a very distinct feature for this mechanism as compared to other types of common conduction mechanism in semiconductors.

4.1.3 Common Conduction Mechanisms in Oxide Ferroelectrics

In the previous two sections most relevant interface and bulk limited conduction mechanisms in semiconductor materials were reviewed. As oxide ferroelectrics are also treated as wide band gap semiconductors, these mechanisms need to be considered when their electrical properties and the leakage current mechanisms are investigated. Even though there has been great effort to understand the leakage mechanisms in oxide ferroelectrics, determination of a universal conduction mechanism for ferroelectrics has not been achieved; rather various research groups reported

different types of conduction mechanisms, even for the same ferroelectric material. Some examples are given below to indicate the range of discrepancies reported in literature. Possible reasons for contradicting results are the intrinsic and extrinsic factors related to the crystalline quality, hence, the defect nature of the single/poly crystalline films as well as the type of the electrodes used in the MFM structures [33].

As an archetypal ferroelectric material, BaTiO_3 and its derivatives have been studied extensively in order to establish the basics for oxide ferroelectrics. Regarding the electrical characterization, space charge limited conduction (SCLC) and Schottky emission were reported in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films [34,35]. On the other hand, in the parent compound, BaTiO_3 , hopping conduction² was claimed to be the dominant conduction mechanism in thin films [36]. This shows that slight changes in the chemical composition of the material can result in a dramatic change in the main conduction mechanism.

Lead zirconate titanate (PZT) and its various compositional derivatives have been investigated thoroughly because of their high piezoelectric properties. One of the early reports on the electrical properties claimed that the space charge limited conduction is the dominant mechanism, where even the correct thickness dependence (d^{-3}) was observed [10]. However, reports in the last decade mostly revealed that the conduction in PZT thin film is Schottky emission [2–5]. Temperature variable measurements showed that different conduction mechanisms can prevail in different temperature and voltage regimes. For example, FN conduction up to 130 K and Schottky emission between 250K-350K was observed in PZT thin films. Between 130K-250K, Schottky emission and FN conduction are dominant at low and high voltage regimes, respectively [3]. As Schottky emission is a highly temperature dependent process, its contribution at high temperatures is dominant over FN tunneling conduction. In other words, at low temperatures, when the thermal energy is not high enough to excite the charge carriers to overcome the Schottky barrier, FN conduction is the dominant mechanism where the tunneling process is not dependent on the temperature.

BiFeO_3 thin films drew large attention due to their large polarization and multiferroic properties at room temperature. This has also initiated numerous studies into the electrical properties of BFO. Early studies revealed that the conduction in BFO thin films is space charge limited in pure and Ni^{2+} doped BFO thin films, whereas Ti^{4+} doping caused a field assisted ionic conduction [11]. The defects (especially oxygen vacancies) in the thin films were held responsible for the conduction behavior. And a variation in oxygen pressure during post-annealing led to a shift in conduction mechanism from SCL to PF as the oxygen content was increased [37].

²A bulk limited conduction mechanism, similar to PF. However the difference is that the conduction is not in the conduction band but takes place through hopping of charge carriers between the trap states due to tunneling effect.

Also, Xiao et al. reported a two orders of magnitude lowering in SCL conduction in BFO thin films by post oxygen implantation [12]. These examples clearly show that the amount of oxygen vacancies in BFO thin films plays a crucial role in determining the conduction properties. Moreover, PF emission was also reported as a dominant mechanism at high temperatures in BFO thin films [38–40], indicating that trap states might dominate the electrical properties. Apart from the bulk limited conduction mechanisms, interface controlled conduction was also observed in BFO thin films. For example, Seidel et al. reported Schottky emission and FN tunneling at low and high voltage regimes, respectively [6]. A change in the Schottky barrier with crystal orientation was also reported in BFO thin films [7]. Additionally, a combination of SCL and Schottky emission was reported at low and high voltages in BFO thin films, respectively [8, 9]. Therefore, it is not straightforward to draw conclusions about the true leakage nature of BFO thin films because of the differences in film crystallinity, film orientation, film composition (doped and non-doped BFO), use of different types of substrates (ranging from Si substrates to perovskite substrates such as SrTiO₃ (STO) and DyScO₃ (DSO)) and measurement stacks (i.e. use of different electrode layers). On one hand, studies that reported bulk-limited conduction involved the use of doped BFO thin films [11, 37, 40] and films grown on Si [37] and STO (111) [41] substrates that do not promote growth of highly crystalline BFO thin films. In light of these reports, it can be conjectured that BFO thin films with doping impurities and less crystalline quality contain more defect states so that the conduction is limited by bulk characteristics. On the other hand, studies that reported interface-limited conduction in BFO thin films appear to involve highly crystalline films. BFO thin films are mostly grown on STO (001) [7–9] or DSO (110)_o [6] substrates with SrRuO₃ electrode layers. This indicates that conduction in films with high crystalline quality (i.e. less defects) seems to be governed by the interface properties.

Due to the Schottky barrier formation at the metal-semiconductor interface, Pintilie et al. [42] and Hrib et al. [4] studied the effects of the electrode layer in detail, confirming that the interface plays a crucial role in the conduction properties of MFM structures. Another important factor that has to be considered while analyzing oxide ferroelectrics is the presence of interface charges due to the spontaneous electrical polarization that does not exist in the non-polar semiconductors. These were not taken into account in most of the semiconductor interface theories. Pintilie and Alexe [14] improved the classical Schottky model by including the effects of the ferroelectric polarization. Moreover, this effect is considered to be so large in BFO thin films that it is held responsible for the resistive switching effect, i.e. the overall conduction is dependent on the polarization direction [5, 20, 41, 43–47]. Unfortunately, there is no consensus on the conduction mechanism in oxide ferroelectrics.

4.1.4 Motivation and structure of the chapter

Regarding the conduction mechanisms in BFO thin films two important questions are addressed in this chapter. (i) How can the electrode layers affect the conduction behavior and is it possible to reduce the leakage current in BFO thin film stacks by using different electrodes? (ii) How can surface termination of the electrode layer affect the electrical properties, either by modifying the electrode surface properties or by modifying the BFO film growth. In order to shed light on the electrode layer, BFO thin films were grown on $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) thin films and 0.5 w% Nb doped STO (Nb:STO) substrates as electrode layers. LSMO and Nb:STO electrodes will create different interfaces with BFO due to their different metal work functions while the top electrode (AFM tip) was kept the same in the MFM structure. If the conduction is mainly interface limited, differences in conduction measurements can be attributed to changes in the bottom electrode layers. In addition to the electrode layers, the influence of substrate/bottom electrode layer surface termination on the conduction properties of BFO thin films was investigated for the following reasons. As shown in chapters 2 and 3, the surface termination changes the growth kinetics, thus, the growth of BFO thin films. BFO films on B-site Nb:STO surfaces consist of smaller domains with rougher surface topography in comparison to BFO thin films on A-site Nb:STO substrates. This indicates that the amount and distribution of defects might differ in these films due to growth conditions, resulting in possibly changes in electrical properties. Further it was already shown that the Schottky barrier between SrRuO_3 thin films and Nb:STO substrates depends on the substrate surface termination [48]. Due to the polar nature of BFO thin films, a similar effect might be observed in BFO thin films. Therefore A- and B- site terminated $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ thin films and Nb doped SrTiO_3 substrates as bottom electrodes for BFO thin films were investigated to reveal the surface termination effects on the conduction behavior.

4.2 Experimental

The results presented in this chapter are based on the measurements from four types of samples, namely Sample 1: BFO/LSMO/STO, Sample 2: BFO/SrO/LSMO/STO, Sample 3: BFO/Nb:STO and Sample 4: BFO/SrO/Nb:STO. Specific termination sites are achieved as following: STO and Nb:STO substrates were chemically treated to achieve B-site termination and SrO deposition was done by pulsed laser interval deposition as described in chapter 2. LSMO electrode layers were grown on B-site terminated STO (001) substrates, which makes the LSMO layer B-site terminated. On such LSMO layers, a single unit cell thick SrO layer was deposited to make the LSMO layer A-site terminated. LSMO thin films were

deposited under an oxygen pressure of 0.24 mbar with a laser repetition rate of 1 Hz whereas BFO thin films were deposited from a stoichiometric target at 0.3 mbar O₂ with a laser repetition rate of 4 Hz. For both LSMO and BFO thin film growths, the rest of the growth parameters were kept the same with an energy density of 3.2 J/cm², a substrate temperature of 670°C and a target-substrate distance of 55 mm.

Conductive atomic force microscopy (C-AFM) and current-voltage (I-V) spectroscopy measurements were carried out by using an Omicron VT-AFM under ultra-high vacuum conditions (with a base pressure in the range of 1×10^{-10} - 5×10^{-9} mbar). For temperature dependent measurements, the samples were mounted to the Omicron cooling sample holder where the heating is provided by a heating element in the cryostat stage and the temperature is monitored by a silicon diode sensor on the sample side of the cryostat stage. This provides the opportunity to work at moderately elevated temperatures (in the range of 300K-400K). In all C-AFM and I-V measurements, diamond-like carbon coated probes, ContDLC from NanoAndMore GmbH, were used because these probes can provide enough resistance against wear and deformations during high temperature measurements in vacuum.

During acquisition of the I-V measurements, the following criteria were taken into account. In order to avoid measuring the displacement current due to polarization switching, the entire regime of the I-V spectroscopy measurements (-10V to +10V) was measured in two steps (from -10V to 0V and from +10V to 0V). In each step, the initial voltage was applied for 2 seconds to stabilize the current (either -10V or +10V, depending on the measurement step), then the voltage sweeping was started. Each spectrum was acquired with 256 data points (with voltage steps of 10V/256). The raster time was set at 15 milliseconds for each data point. However, the current data was recorded after a 12 milliseconds delay time in order to avoid the transient effects regarding the electronics. I-V measurements were taken in the grid-measurement mode of the Omicron-Matrix software. This refers to the measurement mode in which a specified area is divided into equal spaces in both X and Y scan directions where the C-AFM probe visits each intersecting spot in the grid area and takes the I-V spectrum measurement. For the measurements performed in the scope of this chapter, the measurement area was set as $2 \times 2 \mu\text{m}^2$ and 64 measurement points were visited for each set of data and their average was given as the representative I-V spectrum. In order to reveal the temperature dependence of the I-V characteristics of the samples, measurements were performed at five different temperatures from 300K to 400K with a temperature interval of 25K.

4.3 Results and Discussion

4.3.1 BiFeO₃ thin films on La_{2/3}Sr_{1/3}MnO₃ electrode layers

LSMO is an important perovskite oxide material due to its electrical and magnetic properties [49,50] and it has been used in BFO thin film stacks for the following reasons. First, LSMO can be used as a bottom electrode layer because of its conducting properties [51,52]. More interestingly, it can be incorporated in the film stack to create an exchange bias between ferromagnetic LSMO and anti-ferromagnetic BFO so that novel magnetic devices can be developed [53–55]. For proper analysis of such devices, it is important to understand their electrical properties, regarding the contributions of BFO thin films and LSMO electrode layers. Therefore 60 nm thick BFO thin films were grown on MnO₂-terminated (B-site)³ and SrO-terminated (A-site)⁴ LSMO electrode layers (5 nm thick) on STO (001) substrates. RHEED monitoring of thin film growth ensured the targeted thicknesses for BFO, LSMO and SrO layers (data not shown). C-AFM scanning measurements are shown in Figure 4.2 where +3V and +4V of DC voltage was applied to the tip while the surface was scanned. Obviously as the DC voltage is increased higher current was measured from the sample, see Fig 4.2 (a,c) versus (b,d). On the one hand, for both samples higher conducting regions seem to be the domain walls, as discussed in more detail in chapter 5. On the other hand, the BFO sample on A-site terminated LSMO layer shows a higher conductivity compared to the BFO sample on B-site terminated LSMO layer, see Fig. 4.2 (a,b) versus (c,d). In order to understand the electrical properties of BFO samples on A- or B- site terminated LSMO electrode layers, temperature dependent I-V spectroscopy measurements were carried out, as shown in Fig. 4.3. From the linear plots of the I-V spectra of BFO thin films on A- and B-site terminated LSMO (Fig. 4.3 a and c, respectively), it is revealed that the Tip-BFO-LSMO (MFM) system shows a diode like behavior. A higher current is measured for a positive tip bias compared to that of negative tip bias. In additional, the BFO thin film on A-site terminated LSMO shows an order of magnitude higher conductivity for the positive tip bias. In contrast, for negative tip bias, logarithmic plots of the data (b and d) show that the current measurements for both A- and B-site terminated LSMO are nearly the same for the complete applied voltage range.

The positive tip bias side of the I-V spectra measurements for BFO samples on A-site and B-site LSMO electrode layers were plotted in constant temperature representation according to the definitions given in the introduction section. The results are shown in Fig. 4.4.⁵ For SRS and PF emission representations, the curves

³Sample 1: BFO /LSMO/ STO

⁴Sample 2: BFO /SrO / LSMO/ STO

⁵For the negative tip bias side, a similar procedure was applied, however, the data is not shown here.

Figure 4.2: C-AFM imaging of BFO/LSMO/STO and BFO/SrO/LSMO/STO samples in upper and lower rows, respectively. During the imaging +3V and +4V tip bias is applied for (a,c) and (b,d), respectively. The lateral scale bar shown in (d) is valid for all the images. Vertical scale bars are shown separately for each image.

Figure 4.3: Grid I-V measurements on a $2 \times 2 \mu\text{m}^2$ area in a temperature range of 300K to 400K for BFO/LSMO/STO and BFO/SrO/LSMO/STO samples in upper and lower rows, respectively. The results are shown in linear (a,c) and logarithmic (b,d) scales.

for different temperatures nearly overlap at high voltages with a linear relationship between the x and y axes. A linear fit is applied at the high voltage regime in SRS and PF representations in order to calculate its slope, from which ϵ_r is extracted. For the BFO sample on the B-site terminated LSMO electrode, ϵ_r is estimated as 2.2 and 8.9 for SRS and PF representations, respectively, see Table 4.1. For the BFO sample on the A-site terminated LSMO electrode layer, ϵ_r is estimated as 3.4 and 13.6 for SRS and PF representations, respectively. The FN representation of the I-V measurements on both samples reveals that the temperature dependence of the conduction in these samples cannot be ignored, hence, FN tunneling cannot be the main conduction mechanism. Moreover, the SCL representation of the I-V measurements reveals slopes of 5.60 and 5.05 for BFO samples on B- and A-site terminated LSMO electrode layers that do not match with the expected slope of 2. Therefore these results indicate that SRS and PF conduction mechanisms are more probable than FN and SCL mechanisms to be the dominant conduction mechanism in BFO thin film stacks.

In order to estimate the Schottky barrier height at the LSMO electrode-BFO and tip electrode-BFO interfaces, the formalism described in the introduction section was used, see page 62. Firstly, the constant voltage representation of the I-V measurements was plotted, as shown in Fig. 4.5 (a,c,e,g). A linear fit was applied to connect the data points at the same voltage for different temperatures as shown in Fig. 4.5(b,d,f,h). The slope of this linear fit gives the apparent Schottky barrier height ($\phi_{app} = \phi_B - \sqrt{qE/4\pi\epsilon_r\epsilon_0}$). Linear extrapolation to zero Volts gives the Schottky barrier height values ϕ_B : For the BFO sample on B-site LSMO electrode layer, it is 0.26 eV at the LSMO-BFO interface and 1.32 eV at the tip electrode-BFO interface. For the BFO sample on A-site LSMO electrode layer, it is 0.19 eV at the LSMO-BFO interface and 1.29 eV at the tip electrode-BFO interface, also given in Table 4.1.

4.3.2 BiFeO₃ thin films on Nb:SrTiO₃ substrates

In order to unravel the role of the electrode layer in MFM structures, a different bottom electrode layer was used maintaining the same top interface (tip electrode-BFO). As a replacement for the LSMO electrode layer, an Nb:STO substrate was preferred for the following reasons; (i) there is an interest to study BFO thin films without any other magnetic layer in the film stack such as LSMO or SrRuO₃; (ii) to investigate the influence of the growth conditions on electrical properties, Nb:STO substrates offer a platform for which the surface termination was shown to be a significant factor in the growth of BFO thin films as shown in chapter 2. C-AFM was used to probe the conduction map of the BFO samples on Nb:STO substrates, as shown in Fig. 4.6. These images lead to the following findings: as expected, a higher

Figure 4.4: Representations of the I-V measurements, shown in Fig. 4.3, for different conduction mechanism. Upper and lower rows are for BFO/LSMO/STO and BFO/SrO/LSMO/STO samples, respectively. (a,e) SRS emission, (b,f) PF emission, (c,g) FN tunneling, (d,h) SCL conduction representations. The legend for color of lines is given in (a) and holds for all figures.

Figure 4.5: Plots for calculating the Schottky barrier height for BFO/LSMO/STO and BFO/SrO/LSMO/STO samples in upper and lower rows, respectively. (a,e) Constant voltage representation of the I-V measurements and (b,f) $\phi_{apparent}$ vs. $V^{1/2}$ for positive tip bias direction (i.e. LSMO electrode-BFO interface). (c,g) Constant voltage representation of the I-V measurements and (d,h) $\phi_{apparent}$ vs. $V^{1/2}$ for negative tip bias direction (i.e. tip electrode-BFO interface).

Sample name	ϕ_B Bottom electrode - BFO (eV)	ϕ_B Tip electrode - BFO (eV)	ϵ_r from SRS fitting	ϵ_r from PF fitting
1:BFO/LSMO/STO (BFO on B-site LSMO)	0.26 ± 0.07	1.32 ± 0.13	2.2 ± 0.3	8.9 ± 1.4
2:BFO/SrO/LSMO/STO (BFO on A-site LSMO)	0.19 ± 0.03	1.29 ± 0.12	3.4 ± 0.5	13.6 ± 2.1
3:BFO/Nb:STO (BFO on B-site Nb:STO)	0.51 ± 0.05	0.26 ± 0.06	2.9 ± 0.2	11.9 ± 1.0
4:BFO/SrO/Nb:STO (BFO on A-site Nb:STO)	1.10 ± 0.15	1.40 ± 0.25	7.3 ± 3.2	29.3 ± 12.9

Table 4.1: Estimated values for Schottky barrier at the bottom electrode-BFO and tip electrode-BFO interface as well as the optical dielectric constant, extracted from the SRS and PF fittings for all four types of samples.

tip voltage gives rise to a higher conduction in BFO thin films with an enhanced conduction observed at the domain walls. Comparison between the BFO samples grown on B- and A-site terminated Nb:STO substrates shows that relatively higher conduction occurs on B-site terminated Nb:STO.

Results of the I-V measurements performed in the range of 300K-400K are shown in Fig. 4.7 in linear scale (a,c) and in logarithmic scale (b,d). For all temperatures, a lower conduction is observed in BFO thin films on A-site terminated Nb:STO, especially around room temperature. This matches with the C-AFM mapping in Fig. 4.6. In addition, diode-like behavior is similar to the BFO films grown on LSMO electrode layers.

In order to determine the conduction characteristics of these samples, I-V measurements were translated into constant temperature representation as shown in Fig. 4.8. For the BFO thin film on B-site terminated Nb:STO, SRS emission representation shows the best overlapping of the curves at different temperatures. From the linear fit of these curves at the high voltage regime ($> 5V$), ϵ_r is estimated as 2.9. PF emission representation shows that the curves fall at different positions even though they share a similar slope for the linear part. From a linear fit in the high voltage regime, ϵ_r is estimated as 11.9. For FN representation, there is no overlap between the curves for different temperatures and SCL representation reveals a slope of 6.48 which is unrealistic for the SCL conduction. For the BFO thin film on A-site terminated Nb:STO, SRS emission gives also the best fitting except for the room temperature measurement. From the SRS representation ϵ_r is estimated as 7.3. For PF emission representation, the overlap of the curves for different temperatures is

poor and the linear fit at high voltages gives rise to $\epsilon_r \sim 29.3$. In the FN representation, the temperature dependence of the conduction is obvious, therefore FN tunneling cannot be the main conduction mechanism. For SCL representation, two different slopes are obtained as 6.14 and 2.83 at 300K and 400K, respectively. These values are far from the ideally expected slope of 2, indicating SCL is not the main conduction mechanism in these samples.

Assuming that the SRS emission is the main conduction mechanism in these samples, constant voltage representations of the I-V measurements were plotted as shown in Fig. 4.9. According to the formalism, described in the introduction section and similarly applied for BFO thin films on LSMO electrode layers, Schottky barrier heights are calculated. For the BFO thin film on B-site terminated Nb:STO substrate it is 0.51 eV for the Nb:STO-BFO interface and 0.26 eV for the tip electrode-BFO interface. For the BFO thin film on A-site terminated Nb:STO substrate it is 1.10 eV for the Nb:STO-BFO interface and 1.40 eV for the tip electrode-BFO interface. Schottky barrier values and optical dielectric constants are also summarized in Table 4.1.

4.3.3 Discussion

In this chapter, the main conduction mechanism in BFO thin films was investigated in addition to the role of the electrode layer and the surface termination on the conduction properties. I-V measurements on four types of samples propose that SRS emission is most probably the main conduction mechanism due to the following observations:

- I-V measurements show a temperature dependence, implying that thermal excitation plays a crucial role in the conduction mechanism. In this aspect SRS emission and PF emission are probable mechanisms.
- For all samples a diode-like behavior is observed. Resistance for negative tip bias is higher than that for positive bias. This asymmetric behavior is attributed to the different electrode materials at the top and bottom sides, indicating an interface controlled conduction.
- Comparing the BFO samples on the LSMO electrode and the Nb:STO electrode, it is observed that for negative tip bias direction the conductivity vs. voltage behavior is very similar for all four types of sample. However, for positive tip bias, the conduction is lower for BFO samples on Nb:STO substrates. This again shows that the conduction is interface limited. Additionally, this behavior indicates that for negative tip bias, the same type of interface (tip electrode-BFO interface) is probed; while for positive bias a different type of interface is probed in various samples (bottom electrode-BFO interface).

Figure 4.6: C-AFM imaging of BFO/Nb:STO and BFO/SrO/Nb:STO samples in upper and lower rows, respectively. During the imaging +6V, +7V and +8V tip bias is applied for (a,d), (b,e) and (c,f) respectively. The lateral scale bar shown in (f) is valid for all the images. Vertical scale bars are shown separately for each image.

Figure 4.7: Grid I-V measurements on a $2 \times 2 \mu\text{m}^2$ area in a temperature range of 300K to 400K for BFO/Nb:STO and BFO/SrO/Nb:STO samples in upper and lower rows, respectively. The results are shown in linear (a,c) and logarithmic (b,d) scales.

Figure 4.8: Representations of the I-V measurements, shown in Fig. 4.7, for different conduction mechanism. Upper and lower rows are for BFO/Nb:STO and BFO/SrO/Nb:STO samples, respectively. (a,e) SRS emission, (b,f) PF emission, (c,g) FN tunneling, (d,h) SCL conduction representations.

Figure 4.9: Plots for calculating the Schottky barrier height for BFO/Nb:STO and BFO/SrO/Nb:STO samples in upper and lower rows, respectively. (a,e) Constant voltage representation of the I-V measurements and (b,f) $\phi_{apparent}$ vs. $V^{1/2}$ for positive tip bias direction (i.e. Nb:STO electrode-BFO interface). (c,g) Constant voltage representation of the I-V measurements and (d,h) $\phi_{apparent}$ vs. $V^{1/2}$ for negative tip bias direction (i.e. tip electrode-BFO interface).

- The theoretically estimated optical dielectric constant for BFO thin films is 6.86 [56]. Comparison between the estimated values from the high voltage fittings of SRS and PF emission representations do not accurately conclude which fitting gives a more realistic number. However, PF emission fittings overestimate ϵ_r for BFO thin films, especially in the case of BFO on A-site Nb:STO. Therefore, SRS emission appears to be the more plausible conduction mechanism in these films at higher voltage.
- The model developed for the PF emission assumes that the semiconductor layer is connected to the main electrical circuit with ohmic contacts on both sides. This is expected to result in a symmetric I-V spectrum upon a change in the voltage polarity. As the I-V measurement results are far from this ideal condition for PF emission fitting, it is more likely that the dominating conduction mechanism is SRS emission in these films.
- A temperature dependence in I-V measurements exists for all samples. As mentioned in the introduction, FN tunneling is independent of the temperature, hence, it cannot be the main conduction mechanism.
- For SCL representation, the estimated slopes for all samples are far from the ideal value of 2. Therefore, it is not likely that the main conduction is SCL in our samples.

Therefore, SRS emission is the main contributor to the conduction in these BFO thin films for $V > 1.5\text{-}2$ Volts, hence, the analysis for calculating the Schottky barrier height is useful to discover the interface properties. In the Schottky-Mott limit, the barrier height is estimated based on the difference between the electrode work function and the ferroelectric electron affinity according to Equation 4.1. For LSMO and Nb:STO, there has been a significant effort in measuring their work functions and they were reported as 4.8 eV [57–59] and 4.01-4.2 eV [59–61], respectively. The work function of the top electrode was estimated as 4.2 eV [62]. For BFO, the electron affinity was estimated as 3.3 eV by Clark et al. [63].⁶ Using these numbers, the estimated Schottky barrier heights at the Schottky-Mott limit are 1.4 eV, 0.7-0.9 eV and 0.9 eV at the LSMO-BFO, Nb:STO-BFO and top electrode-BFO interfaces, respectively. The experimentally measured Schottky barrier heights do not match these estimates. This indicates that other factors such as the formation of an interfacial layer, interface states and polar structure of the materials might play a role rather than a simple Schottky barrier formation.

⁶It is important to mention that Clark et al. estimated this value based on the electron affinity of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films because the conduction band is formed by Bi p states in both materials. Although many studies [18,64,65] used this value as the electron affinity of BFO, to our knowledge, experimental proof is still missing. Therefore, one has to be careful when making assumptions based on this electron affinity value.

In order to understand the electrical properties of MFM structures, possible energy band alignments are considered between the top/bottom electrodes and BFO thin films treating BFO as an *n*-type or *p*-type semiconductor. The true nature of BFO is not exactly known. It was claimed to be *p*-type due to Bi deficiencies [18] and *n*-type due to oxygen vacancies [19,20]. Here we treat both the top and bottom electrode as a metal layer. Firstly, because the boron doped diamond-like carbon AFM probes show highly metallic behavior [66] and secondly, a 5 nm thick LSMO was shown to have metallic properties [67]. Thirdly, the Nb doped STO substrate, depending on the doping level, can also be assumed to be metallic due to its high conductivity [68,69]. Additionally, 0.1 w% Nb:STO was shown to have an ohmic contact with Au electrode layers [70], indicating that the Nb:STO-Au interface is a metal-to-metal contact. Therefore, it is reasonable to assume that the 0.5 w% Nb:STO substrate acts as a metal layer in the analysis of BFO thin film structures. Taking these assumptions on the work function and electron affinity values into account, two possible band diagrams are proposed in Figure 4.10. In this schematic, (a) represents the energy band diagram of the MFM structure with BFO as an *n*-type semiconductor, whereas (b) assumes a *p*-type BFO semiconductor. In the case of *n*-type BFO, electrons are the majority charge carriers and they are transferred from BFO to the electrode layers upon formation of metal-semiconductor interface to reach an equilibrium that is driven by the difference in metal work functions and BFO electron affinity. As the electrons are depleted in the vicinity of electrode layers, BFO conduction and valence bands are bent upward. In the case of *p*-type BFO, holes are the majority carriers and they move from the BFO layer into the metal layers. That results in a downward band bending. It is noted that these MFM structures are considered as two back-to-back Schottky diodes. Especially, this is different from the case that Nb:STO is considered an *n*-type semiconductor. This would lead to *pn* or *nn*⁺-type heterojunction diodes [18,65] that do not form a Schottky barrier at the interface.

When two back-to-back Schottky diodes are considered under an applied voltage, it is important to distinguish which interface controls the overall conduction behavior of the MFM structure. In the case of *n*-type BFO, a positive tip bias causes electrons to be injected from the bottom electrode, facing the Schottky barrier at the bottom electrode-BFO interface. In contrast, a negative tip bias results in an electron injection from the top electrode into the BFO film, facing a Schottky barrier at the tip electrode-BFO interface. Therefore, the conduction is limited by the bottom electrode-BFO interface (ϕ_{e1}) and top electrode-BFO interface (ϕ_{e2}) as shown in Figure 4.10(a) for positive and negative tip biases, respectively. In the case of *p*-type BFO, a positive tip bias causes holes to move from the top electrode to the BFO film, facing a barrier height of ϕ_{h2} . On the other hand, negative tip bias moves the holes

Figure 4.10: Energy band diagram schematics of Bottom electrode-BFO-Top electrode (MFM) structures. (a,b) represents the case of BFO being *n*-type and *p*-type semiconductor, respectively.

from the bottom electrode to the BFO film for which they have to cross a barrier of ϕ_{h1} , see Figure 4.10(b). Hence, the conduction is limited by the top electrode-BFO interface and bottom electrode-BFO interface for positive and negative tip bias, respectively. In this regard, the most important clue, that can help to distinguish which interface is the limiting factor in I-V spectroscopy measurements, is that the tip electrode-BFO interface should consistently give similar Schottky barrier value for all samples. Comparing the results of I-V spectroscopy measurements on LSMO and Nb:STO electrodes, it can be concluded that the Schottky barrier height that is extracted from the negative tip bias part is nearly equal for all measurements.⁷ This is the case when BFO is an *n*-type semiconductor and upon application of negative tip bias, ϕ_{e2} is the limiting Schottky barrier. Therefore, it can be concluded that these BFO samples are *n*-type semiconductors. This can arise from the possible existence of oxygen vacancies. Regarding the tip electrode-BFO interface, higher Schottky barrier heights are estimated compared to the bottom electrode (i.e. LSMO or Nb:STO)-BFO interfaces. This also coincides with the observed diode-like behavior.

For BFO thin films on LSMO electrode layers, the trends observed in C-AFM mapping match well with the calculated Schottky barrier heights. BFO thin films on A-site terminated LSMO electrode layers show a higher conduction when the barrier at the LSMO-BFO interface is lower than in the case of the B-site sample. For BFO thin films on Nb:STO substrates there is also a good match between the estimated Schottky barrier heights for Nb:STO-BFO interfaces and C-AFM mapping. For BFO thin films on A-site terminated Nb:STO substrates, a larger Schottky barrier is esti-

⁷These results are shown in Table 4.1 in the column for Tip electrode-BFO interface already with fairly similar values except for the BFO sample on B-site Nb:STO for unknown reasons. In the results section, assigning the positive and negative tip bias directions to the correct interfaces was done without giving this analysis yet for the sake of clarity.

mated, thus, it conforms to the lower conduction observed in C-AFM. Additionally, higher Schottky barrier heights observed for Nb:STO-BFO interface do explain well why a higher tip DC bias is required for C-AFM mapping compared to the BFO thin films on LSMO electrode layers.

It is surprising that the introduction of the single SrO layer does not result in the same behavior for BFO thin films on LSMO and Nb:STO electrodes. In the case of LSMO electrodes, it lowers the Schottky barrier height whereas in the case of Nb:STO, it significantly increases the Schottky barrier height. In the bulk of the LSMO electrode layer, an A-site atomic plane consists of La (2/3) and Sr (1/3) and oxygen atoms, whereas the deposition of SrO single layer creates a top A-site atomic plane consisting of only Sr and oxygen atoms. This change in La:Sr ratio at the top atomic plane of LSMO also affects the nearest MnO₆ octahedra by reducing its conducting behavior. Therefore, it is expected that the Schottky barrier is increased in the non-doped and defect free interface case. However, the overall Schottky barrier values are far from matching the theoretically estimated values. In other words, the Schottky-Mott limit barrier height is expected to be in the range of 1.4 eV whereas the measured values are around 0.2 eV. This indicates that local defects and surface states play a crucial role at the LSMO-BFO interface. On the other hand, the role of the SrO layer might be more effective in BFO thin films on Nb:STO substrate. It is shown in chapter 2 that a SrO layer improves the growth of BFO thin films from the initial stage and may prevent the formation of surface states at the Nb:STO-BFO interface. This can allow the interface to behave more in the Schottky-Mott limit and facilitates the formation of a higher Schottky barrier at the BFO-Nb:STO interface.

4.4 Conclusion

In this chapter, the influence of the electrode layer and the surface termination on the leakage current in BFO thin film stacks was investigated. It was shown that the main conduction mechanism for high voltage regime in these BFO thin film stacks is SRS emission and the choice of the electrode material makes a significant difference in the electrical properties. BFO thin films on LSMO electrode layers show an order of magnitude higher conduction compared to BFO thin films on Nb:STO substrates. Especially for applications that require low leakage current and absence of other magnetic layers, Nb:STO substrates can be a good option as an electrode layer. BFO thin films grown on A-site terminated Nb:STO substrates have the highest Schottky barrier height (1.1 eV) among all four types of samples investigated. In addition, the surface termination of the bottom electrode layer was also shown to provide changes in the Schottky barrier, either by influencing the surface properties

of the LSMO electrode layer or by changing the growth conditions of the BFO layer, thus, the electrical properties of BFO thin film stacks. In this study the dependence of the Schottky barrier height in BFO thin film stacks on the surface termination, especially in the case of Nb:STO substrates, was shown for the first time. It is important to emphasize that especially for applications that make use of ultra-thin BFO films, the influence of the surface termination might be even larger. In summary, it is revealed that the conduction in BFO thin film stacks is highly dependent on the interface. Any factor that changes the interface characteristics, such as the electrode layer or surface termination, can influence the interface transmission properties. Therefore, the interface has to be given special attention when designing BFO thin film applications using the electrical properties of the BFO film.

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Chapter 5

Preferential domain wall conductivity in BiFeO_3 thin films

Abstract: Domain wall conductivity is a controversial subject in the study of ferroelectric materials. Although it has been shown in several materials systems, the origin of domain wall conductivity and factors influencing it are still under debate. In this chapter, the origin of domain wall conductivity was studied in 71° domain walls of BiFeO_3 thin films on Nb doped SrTiO_3 (001) substrates by conductive atomic force microscope (C-AFM). Current vs. voltage (IV) spectroscopy measurements revealed that abrupt jumps are observed in higher voltage regime ($> 6\text{V}$) due to trap centers in the band gap. It is claimed that these trap centers arise from oxygen vacancies and are held responsible for the enhanced domain wall conductivity. Moreover, the electrical conduction behavior of charged domain walls in BiFeO_3 thin films on TbScO_3 (001)_o was investigated by sequential C-AFM and piezoresponse force microscopy (PFM) imaging. These measurements demonstrates a preferential enhanced domain wall conductivity in which head-to-head domain walls are proposed to be more conducting than tail-to-tail domain walls due to preferential accumulation of electrons to screen the positive polarization charges.

5.1 Introduction

Technological advances in scanning probe microscopy [1–5] and transmission electron microscopy [6] in the last decades have led to a significant progress in the study of domain walls, thus, enabled the discovery of various emergent phenomena at spatially confined areas. Among interesting examples of such phenomena are the discovery of superconductivity at twin domain walls of WO₃ [7], enhanced resistivity in phosphates [8], ferroelectrically polarized domain walls in paraelectric SrTiO₃ [9] and electrical conductivity at domain walls of ferroelectric BiFeO₃ (BFO) thin films [10,11]. Recently, this has attracted much attention as it can pave the way towards domain wall nanoelectronics [12]. Furthermore, as the size of individual components in electronic devices keep shrinking, domain walls will become technologically more important because of their small size (about a few unit cell wide) [13] and control over their location [10].

Although domain wall conductivity was already theoretically predicted in 1973 [14], it took about 40 years to experimentally prove it. Seidel et al. [10] showed for the first time domain wall conductivity in artificially written 109° and 180° domain walls of BFO thin films. This has initiated numerous studies that later showed existence of electrical conductivity also in as-grown 109° [15] and 71° [11] domain walls of BFO. In contrast to the belief that domain wall conductivity was peculiar to BFO, observation of domain wall conductivity in other ferroelectric materials such as Pb(Zr_{0.2}Ti_{0.8})O₃ (PZT) [16], LiNbO₃ [17] and hexagonal manganites [18,19] has suggested the existence of a more universal phenomenon. Even though domain wall conductivity is common in various ferroelectric materials, there is no single mechanism behind its origin. Non-existence of such a single mechanism arises due to the differences in the nature of domain walls in different ferroelectric materials as well as the differences in growth and processing of same type of ferroelectric samples across various labs. However detailed understanding of the rich physics behind domain wall functionality is required to realize the use of domain walls as an active entity in electronic devices. In this chapter, a summary of possible mechanisms for the origin of domain wall conductivity is given firstly. Subsequently, various types of BFO thin films are being studied to determine the relation between structural domain wall formation and local conductivity.

5.1.1 Origin of Domain Wall Conductivity

Domain wall conductivity in ferroelectrics has been observed mostly in correlated oxide systems. In ferroelectric oxide systems, the following factors play a role in the emergence of domain wall conductivity:

- Structural changes in the vicinity of domain walls

- Polarization changes in the vicinity of domain walls
- Growth and processing conditions of ferroelectric materials

Structural changes are held responsible for domain wall conductivity from two perspectives: (i) variation in local electronic band gap due to structural changes and (ii) accumulation of defects, in particular, oxygen vacancies due to strain gradient. Experimental observation of the enhanced domain wall conductivity in BFO thin films was acclaimed to the lower local band gap at the domain wall [10]. Reduction in the band gap at domain walls was further supported by theoretical and experimental studies. Theoretical calculations have put forth the Fe-O-Fe bond straightening at 109° , 180° and 71° BFO domain walls, from highest to lowest respectively [10,20] and strain gradients [21,22] as causes of lowering in the band gap. These results were later supported by scanning tunneling microscopy spectroscopy measurements in cross-sectional samples (similar to TEM specimens) [23]. Additionally, accumulation of oxygen vacancies in the vicinity of domain walls due to strain gradient was also proposed to be a driving force for enhanced conductivity by lowering the Schottky barrier between the sample and the AFM tip [24].

The effects of structural and polarization changes in the vicinity of domain walls are often interlinked as their order parameters are coupled to each other in multiferroic materials. BFO is a well known example where 71° and 109° domain walls are both ferroelastic and ferroelectric while 180° domain walls are purely ferroelectric. However, the crystal structure of ferroelectrics determine the domain wall plane, thus, the normal component of polarization vector to the domain wall (i.e. polarization discontinuity). DFT calculations have put forth that an electrical potential drop may arise in the vicinity of domain walls, so it can attract charge carriers to screen the polarization discontinuity [10,20]. The amount of potential drop across different types of domain walls is also in agreement with the domain wall conductivity observations of Seidel et al. [10]. Moreover, domain wall conductivity is also observed in pure ferroelectric 180° domain walls of tetragonal $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ [16] thin films where there are no structural changes and the normal component of the polarization to the domain wall plane is non-zero. Although stabilization of inclined domains is not favorable, it can form during polarization switching and be stabilized by charged defects [25]. It is claimed that segregation of charged defects at inclined domain walls can be the reason for enhanced conductivity in written domain walls of PZT.

Effects of polarization changes on domain wall conductivity becomes even more important in the case of charged domain walls i.e. head-to-head and tail-to-tail domain walls. On the one hand, vortex-like charged domain walls were artificially written and stabilized in BFO thin films and reported to show enhanced conductivity due to the coupled response of polarization and electron mobile vacancy subsystems with

external bias [26]. On the other hand, charged domain walls in as-grown ferroelectrics are usually observed in topologically protected hexagonal manganites [27–29]. In p-type hexagonal manganite ferroelectrics, tail-to-tail domain walls require accumulation of abundantly present hole charges to screen polarization charges. On the contrary, head-to-head domain walls attract the scarcely found negative charges. Therefore tail-to-tail domain walls were claimed to be more conductive than head-to-head domain walls in ErMnO₃ [19] and in HoMnO₃ [18] hexagonal ferroelectrics. Although polarization discontinuity play an important role, it does not solely determine the domain wall conductivity. Extrinsic growth and processing conditions can contribute to the conductivity as well. As an example, in investigation of hexagonal manganites, it was found that insulating domain walls of YMnO₃ [30] can show conductive behavior when the sample was grown under oxygen deficient conditions [31].

The role of the oxygen vacancies on the domain wall conductivity was also investigated in BFO [15, 24] and PZT [32] thin films. By controlling the oxygen pressure during sample cool down, the domain wall conductivity changed nearly by an order of magnitude. The higher the oxygen vacancies in the BFO sample, the higher domain wall conductivity is observed. This is in line with thermally activated conductivity mechanism of BFO domain and domain walls [15] as oxygen vacancies can act as trap centers in the band gap from where charge carriers can be thermally excited to conduction band. Additionally, accumulation of oxygen vacancies near domain walls is driven by the strain gradients and is acclaimed to lower the Schottky barrier between the AFM tip and the sample [24]. In PZT samples, thermal cycling in ultra-high vacuum and exposure to ambient conditions have successfully created a controlled switching of polarization direction in the entire film due to the intricate balance between the oxygen content of the sample and the screening charges (i.e. adsorbates) on the surface. This has also led to a reversible insulating-conducting behavior at 180° domain walls [32]. Furthermore, Stolichnov et al. has demonstrated that defects are the possible source of conduction in the original position of BFO domain walls after moving the 109° domain walls artificially [33]. Therefore role of defects, particularly oxygen vacancies, should be given a special importance in the discussion for origin of domain wall conductivity.

As briefly described in the aforementioned examples, domain wall conductivity is a complex interplay of structural and polarization changes and defect states in ferroelectrics. Despite the fact that most studies consider a static conductivity [10, 11, 34] at BFO domain walls, Maksymovych et al. studied the hysteresis behavior of domain wall conductivity and concluded that it is a more complex and dynamic phenomenon due to the interaction between the domain walls and extended defects [35].

5.1.2 Motivation of the chapter

The main focus of this chapter is to study the domain wall conductivity and factors influencing it. The first question to address is why the domain walls are more conducting than domains, followed by how the polarization configuration in charged domain walls can influence the domain wall conductivity. Answers to these questions are sought out by studying BFO thin films on Nb doped SrTiO₃ (Nb:STO) (001) and TbScO₃ (001)_o substrates for the following reasons. Since SrO terminated Nb:STO substrates facilitate a reduced leakage current in BFO thin films as shown in chapter 4 due to improved crystallinity, it can possibly reveal more information why domain walls are more conducting than domains. Therefore, local IV spectroscopy measurements in 60 nm thick BFO thin films on SrO terminated Nb:STO (001) were carried out by C-AFM. Additionally, as discussed in detail in chapter 3, as-grown 60 nm thick BFO thin films on SrO terminated 5 nm thick La_{2/3}Sr_{1/3}MnO₃ (LSMO) electrode layers on TbScO₃ (001)_o substrates consist of charged 109° domain walls. The interest for studying domain wall conductivity in these samples is four folded. (i) Domain walls in BFO thin films on TbScO₃ (000)_o substrates are less susceptible to pinning due to structural defects at the interface and meandering nature of domain walls imply that their formation is governed by electrostatics rather than elastic effects. (ii) It is known that geometrical manipulation of written domain walls shows a tunable conductivity along the domain wall with respect to the polarization angle [36]. (iii) Study of charged domain walls is limited to hexagonal manganites in single crystals of YMnO₃, ErMnO₃ and HoMnO₃ [18, 19, 30] whereas it is lacking in thin films that is technologically more interesting (with an exception for TbMnO₃ [37]). (iv) It is predicted that head-to-head domain walls show a higher conductivity than tail-to-tail domain walls in n-type semiconductors [34]. Regarding these aspects, BFO thin films on TbScO₃ (001)_o substrates provide a rich playground to study the domain wall conductivity in 109° domain walls. These are as-grown charged domain walls that can possibly attract oxygen vacancies selectively, thus, leading to a preferential domain wall conductivity.¹

5.2 Results and Discussion

5.2.1 BiFeO₃ thin films on Nb:SrTiO₃ substrates

Conductivity in 71° domain walls of BFO thin films on Nb:STO substrates is shown in Figure 5.1. Even though the observed domain wall conductivity is in agreement with previous studies [11, 24], best conductance contrast in these samples were achieved

¹Experimental details for growth of BFO samples on Nb:STO (001) and TbScO₃ (001)_o substrates can be found in chapters 2 and 3, respectively. Experimental details for C-AFM and IV spectroscopy measurements are given in chapter 4.

with a tip bias of 8V whereas the comparable samples on LSMO electrode layers typically require a tip bias of around 3V. This is probably due to the higher Schottky barrier at BFO-Nb:STO interface (shown in chapter 4). In order to explore the differences between domains and domain walls, IV spectroscopy measurements were performed on several locations and the results are shown in Figure 5.2. Only two single measurements out of more than twenty measurements are shown in addition to the average of all measurements to highlight the details in individual measurements both on domain walls and domains. One of the expected outcome of these measurements is that conductivity in the domain walls (c) is higher than in the domains (f). The individual measurements on domain walls and domains show both similarities and differences. Up to 6V, higher conduction during trace measurement than retrace, known as positive hysteresis, is observed in all measurements on domain walls² and domains. From about 6V on, trace and retrace curves overlap and follow an exponential change on domains (d,e) whereas abrupt jumps are observed on domain walls (a,b), leading to a slight negative hysteresis as can be seen clearly on the average plot (c).

Abrupt jumps in domain wall IV measurements can indicate the origin for the enhanced domain wall conductivity. These jumps can arise from the accumulation of oxygen vacancies in the vicinity of domain walls due to strain gradient [24]. Energy level of these oxygen vacancies can be anywhere in the band gap and they can act as trap centers. As the applied voltage is increased, charge carriers can be freed abruptly from the trap centers, thus, contribute to the domain wall conduction. These trap centers are activated during trace measurement and remains so during retrace measurement, typically leading to a negative hysteresis where the current during retrace measurement is higher than trace measurement as can be seen on the average plot in Figure 5.2 (c). If the trap center in the band gap is to remain at the same level, repetition of the spectroscopy measurement is expected to give the abrupt jumps at the same voltage. However this is not the case in the measurements (data not shown) and behavior of domain wall conductivity is a stochastic process. This can be related to the fact that repetition of the measurement at the same spot may cause a change in the local temperature, thus, thermally activate the charge carriers from the trap centers as well. This means that it is difficult to have a control over the domain wall conductivity due to its unpredictable nature. This is also in agreement with the claims of domain wall conductivity being a more dynamic phenomenon than a static conductivity [35]. Furthermore, defects playing a role in the enhanced domain wall conductivity is also in agreement with previous studies [32,33]. Hence, it can be concluded that the enhanced domain wall conductivity is related to the defects, especially to oxygen vacancies.

²Although the hysteresis exists in the lower voltage regime, it is not visible in (a) because of the scale.

Figure 5.1: C-AFM measurement on BFO (60nm) /SrO/Nb:STO sample. (a) Topography image and (b) conductivity image with an applied tip DC bias of 8V.

Figure 5.2: I-V spectra measurements on 71° domain walls (upper row) and on domains (lower row). (a,b) Measurements taken on different 71° domain wall spots where (c) is an average of I-V measurements taken at more than 20 spots. (d,e) I-V spectra at different domain spots. (f) Average of I-V measurements taken at more than 20 domain spots.

A common feature in the IV-spectroscopy measurements on domain walls and domains is the positive hysteresis that was observed up to nearly 6V. This behavior is quite different than previously observed hysteric IV curves in measurements of BFO thin films [38,39]. As the electronic contribution to the conduction usually give rise to a negative hysteresis (e.g. above 6V on domain walls), another possibility to consider for the observed positive hysteresis is the ionic contribution. During the trace measurement, positively charged oxygen vacancies can migrate towards the negatively biased bottom electrode. If the oxygen vacancies do not migrate back during the retrace measurement, it can explain why a positive hysteresis is observed. On the other hand, repetitive IV measurements on the same spot should have caused a depletion of oxygen vacancies near the top surface, effectively reducing the number of vacancies to migrate further. If this is true, the hysteresis opening is expected to close by consecutive measurements. However, no closing of the hysteresis has been observed in such measurements (data not shown). Impedance measurements can be useful to characterize the ionic conductivity in BFO thin films and possibly give clues about the positive hysteresis.

5.2.2 BiFeO₃ thin films on TbScO₃ substrates

Next to the growth conditions and the defect distribution in thin films, effect of polarization changes near domain walls is an interesting effect to study domain wall conductivity. Therefore, C-AFM measurements were performed on charged 109° domain walls in BFO thin films with LSMO electrode layers on TbScO₃ (001)_o substrates and the results are shown in Figure 5.3 (a,b). In order to reveal the correlation between the domain wall conductivity and polarization changes, PFM measurements were also performed subsequently, see Figure 5.3 (d,e,f). At first sight, it was observed that domain walls appear as closed circles in the PFM in-plane amplitude image (e) whereas in the conduction map (b) closed circles are missing and only one side of the domain walls show enhanced conductivity. Using the particle on the topography images as a reference point,³ conduction map and PFM in-plane amplitude images are overlaid as shown in Figure 5.4. In-plane polarization direction of BFO domains cannot be determined from regular PFM imaging, hence, it is not possible to assign the absolute directions to domains. However, it is known that in-plane polarization is along the <110> direction which coincides with horizontal edge of the image⁴. Therefore, two possibilities are represented in the overlaid image, namely, head-to-head and tail-to-tail domain walls are assigned to more conducting domain walls in the upper and lower part of the image, respectively. Among these possi-

³Between consecutive C-AFM and PFM imaging, tip has to be disengaged to switch the microscope mode that causes a little drift between two sets of images.

⁴Detailed characterization of such domain walls were given in chapter 3.

Figure 5.3: Consecutive C-AFM and PFM imaging on BFO (60nm) / SrO / LSMO (5nm) / TSO (001)_o sample. C-AFM (a) height and (b) conductivity images. (c) Graphical illustration of the sample stack. PFM (d) height, (e) in-plane amplitude and (f) in-plane phase images.

Figure 5.4: Overlaid image of C-AFM conductivity and PFM in-plane amplitude images as taken from Figure 5.3. The image is divided into two parts with a dashed white line where the enhanced conductivity is assigned either to head-to-head or tail-to-tail domain walls in upper and lower parts, respectively.

ble options, head-to-head domain walls are claimed to be more conducting because of the following arguments. Firstly, based on the theoretical predictions of Eliseev et al. [34] head-to-head domain walls are more conducting than tail-to-tail domain walls in n-type semiconductors. Secondly, it was proposed that oxygen vacancies can play a key role for enhanced conductivity in 71° domain walls of BFO thin films. If the defects are predominant factor in domain wall conductivity, positively charged oxygen vacancies are expected to segregate around tail-to-tail domain walls while the corresponding free electrons are driven towards the head-to-head domain walls as depicted in Figure 5.5. As BFO was shown to be an n-type semiconductor in chapter 4, it can be claimed that preferential enhanced conductivity can occur at head-to-head domain walls. It is noteworthy to mention that Eliseev's predictions are for static conductivity of free charge carriers that are segregated at charged domain walls to screen the polarization. Therefore it is expected that domain wall conductivity should increase as the temperature is lowered (similar to metallic conductivity). On the contrary, experimental findings do show an opposite effect and at 120K no domain wall conductivity was observed (data not shown). This supports the idea of a thermally activated conduction mechanism being a dominant factor due to defect states. Therefore, accumulation of electrons that are freed from oxygen vacancies sounds as a more plausible mechanism for enhanced head-to-head domain wall conductivity. In order to pinpoint the exact type of domain walls with preferred conductivity, a polarization switching experiment can be conducted as following. By switching on and off the tip bias during trace and retrace lines during a PFM scan, certain lateral direction can be forced for the in-plane polarization. Once the in-plane polarization of the artificially written area is known, a larger size image can be taken to determine the in-plane polarization direction of as-grown areas.⁵ Subsequent C-AFM measurement on the same area can reveal the exact type of more conducting domain wall type.

5.3 Conclusion

In this chapter, domain wall conductivity in BFO thin films has been investigated from two perspectives. Firstly why the domain walls are more conducting than the domains and secondly whether the charged domain walls result in a preferential domain wall conductivity. It is found that abrupt changes during the IV measurements on domain walls represent the charges being released from the trap centers, thus, lead to enhanced domain wall conductivity. In other words, accumulation of defects, particularly of oxygen vacancies, in the vicinity of domain walls are held responsible for the observed behavior. This finding is in agreement with previously reported

⁵More details of such an experiment was given in chapter 3 on page 47.

Figure 5.5: Schematic representation of charge carriers under the internal electric field of BFO thin film. Upon oxygen vacancy formation ($V_O^{\bullet\bullet}$), positively charged vacancies are driven towards the tail-to-tail domain walls (dw) whereas free electrons accumulate in the vicinity of head-to-head domain walls. In n-type BFO, electrons are the main charge carriers, thus, head-to-head domain walls appear more conducting than tail-to-tail domain walls. Solid arrows represent the polarization vector whereas the dashed arrow represent the internal electric field due to the polarization. Negative and positive charges in the vicinity of the domain walls depict the state of accumulated charge carriers that are formed upon oxygen vacancy formation and migration of charges towards domain walls.

negative hysteresis in IV spectroscopy of BFO thin films [38,39] and dynamic behavior of domain wall conductivity [35]. Next to the hysteresis caused by these abrupt jumps, direct use of Nb:STO substrates as an electrode have facilitated observation of a positive hysteresis in the voltage regime lower than 6V. Further investigation into this positive hysteresis behavior can potentially give a way to understand the ionic conductivity mechanisms in BFO thin films as well. Last but not least, a preferential domain wall conductivity on charged 109° domain walls of BFO thin films on TbScO_3 substrates was observed. Head-to-head domain walls are claimed to be more conducting than tail-to-tail domain walls due to accumulation of electrons to screen the positively charged domain walls. This is the first time observation of preferential domain wall conductivity in as-grown charged domain walls of BFO thin films unlike the artificially written vortex-like charged domain walls [26]. Additionally, this study showed that existence of charged domain walls, along with a preferential domain wall conductivity, is not limited to single crystals [18,19,30] and thin films [37] of hexagonal manganites but can also be found in as-grown BFO thin films. These findings can help in further understanding of the domain wall conductivity in BFO thin films and other oxide ferroelectrics.

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Summary

There has been a tremendous interest in multiferroic materials in the last decades. Coupling between the electrical, magnetic and structural order parameters has been at the core of multiferroic device applications. These coupling effects were aimed to create novel functionalities in nanoelectronics devices. One of the most striking and desired applications of multiferroic materials is in memory devices for data storage. Current hard disks are based on storing data bits in magnetic domains where the up and down oriented domains correspond to fundamental data storage bits of 0 and 1. Reading and writing of magnetic domains are done by application of a magnetic field. Although magnetic data reading is a convenient method, due to its non-destructive nature, data writing by magnetic fields requires the use of a magnetic coil and high currents. This hampers the miniaturization of magnetic domains which is fundamental for creating bits with smaller sizes. In addition, use of high currents to create large enough magnetic fields to switch the state of a data bit causes high heat waste which is also often a detrimental factor to the device performance and lifetime. In order to overcome these issues, multiferroic materials offer a promising direction to write data bits using an electric field whereas read-out can be done by a magnetic field. This has been the most powerful driving force for research into multiferroic materials, especially BiFeO_3 (BFO), which shows coupling between magnetic and ferroelectric order parameters at room temperature. Realization of BFO device applications depends on overcoming the challenges regarding BFO thin film growth and its functional properties. Therefore this thesis focused on unraveling the scientific issues with BFO thin film growth by engineering the interface with the underlying substrate, enabling control over the specific domain formation. Thus it studies the functional properties with a focus on the variation in conducting behavior.

In chapter 2, the surface termination of SrTiO_3 (STO) substrates is shown to change the growth kinetics of BFO thin films. A B-site terminated (TiO_2 atomic plane) STO surface leads to BFO thin film growth with a high nucleation density, resulting in formation of all structural domain variants of BFO with some defects visible on the thin film surface. On the other hand, an A- site terminated (SrO atomic plane) STO surface facilitates step-flow like BFO thin film growth due to the

enhanced surface diffusivity. This results in an increased influence of the substrate surface step edges on the BFO thin film growth and leads to a selectivity among the structural domain variants. BFO thin films on A- site terminated STO consist of two structural variants with domains ordered over a longer range as compared to BFO thin films on B-site terminated STO substrates.

The study of substrate interface effects are extended from surface termination to surface symmetry in chapter 3. BFO thin films grown on TbScO_3 (TSO) $(110)_o$ and $(001)_o$ substrates show existence of different structural variants with significant variations in formation of domains and domain walls. On both substrates, two structural variants of different pairs are predominantly selected due to different symmetry breaking parameters. TSO $(110)_o$ substrates mainly promote the formation of neutral 109° domain walls with very narrow domain widths. Selectivity in structural variants arises due to the non- 90° angle which is positioned along the out-of-plane direction of the TSO $(110)_o$ substrate. On the other hand, TSO $(001)_o$ substrates cause formation of charged 109° domain walls in a meandering shape. In this case, the selectivity in structural variants arises from the fact that the non- 90° angle lies in the substrate surface plane. Differences between the BFO samples on TSO $(110)_o$ and $(001)_o$ substrates clearly show that substrate effects are not only limited to strain, as often considered to be the biggest effect, but that substrate symmetry plays a crucial role in the growth of BFO thin films.

Successful device applications of BFO depend strongly on its electrical properties. Therefore, chapter 4 is devoted to the study of the conducting properties in BFO thin film stacks. Two aspects are considered as influential parameters, namely the electrode layers and the surface termination. As electrodes, $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) and Nb doped STO (Nb:STO) are used. It is shown that a lower Schottky barrier exists at the LSMO-BFO interface, as compared to the Nb:STO-BFO interface. Therefore, a higher conduction is observed in BFO stacks with LSMO electrode layers. With regard to the surface termination, the difference between Schottky barrier values at A- site LSMO-BFO and B- site LSMO-BFO interfaces is very low. In contrast, Schottky barrier at A-site Nb:STO-BFO is nearly twice as at B-site Nb:STO-BFO interface. Interface engineering for BFO thin film stacks enables control of the Schottky barrier at the interface so that device leakage problems can be overcome.

One of the most controversial topics in BFO thin film functional properties is the domain wall conductivity. Chapter 5 shows the results of domain wall conductivity measurements in BFO thin films on Nb:STO and TSO $(001)_o$ substrates. In BFO/Nb:STO samples non-stochastic changes in current are observed during current-voltage measurements. These are claimed to arise from the oxygen vacancies that lie at random levels in the energy band. Moreover, positive polarization charges

are held accountable to gather such oxygen vacancies in the vicinity of head-to-head 109° domain walls in BFO thin films on TSO (001)_o substrates. This leads to the formation of preferential domain wall conductivity in BFO thin films.

Samenvatting

De laatste decennia is een enorme interesse ontstaan in multiferroïsche materialen. Koppeling tussen de elektrische, magnetische en structurele ordeparameters vormt de kern van het toepassen van multiferroïsche materialen in elektronica. Met deze koppelingseffecten worden nieuwe functionaliteiten in nanoelektronica beoogd. Een van de meest opvallende en gewilde toepassingen van multiferroïsche materialen is dataopslag. Hedendaagse harde schijven zijn gebaseerd op het opslaan van databits in magnetische domeinen, waar de naar boven en naar beneden georiënteerde domeinen overeenkomen met de fundamentele databits 0 en 1. Lezen en schrijven van magnetische domeinen wordt gedaan met een magnetisch veld. Hoewel het magnetisch lezen van data een geschikte methode is vanwege het niet-destructieve karakter ervan, vereist het schrijven door magnetische velden het gebruik van magnetische spoelen en hoge stromen. Dit belemmert de miniaturisatie van magnetische domeinen, wat nodig is voor het verkrijgen van bits met kleinere afmetingen. Daarbovenop veroorzaakt het gebruik van hoge stromen, nodig om voldoende hoge magnetische velden te maken om een databit om te schakelen, een groot warmteverlies, wat vaak ook nadelig is voor de prestatie en levensduur van harde schijven. Multiferroïsche materialen bieden een veelbelovende richting om deze kwesties te verhelpen door het schrijven van databits te doen met een elektrisch veld, terwijl uitlezen gedaan kan worden door een magnetisch veld. Dit is de grootste drijvende kracht achter onderzoek naar multiferroïsche materialen geweest, in het bijzonder naar BiFeO_3 (BFO), dat een koppeling tussen magnetische en ferroelektrische ordeparameters heeft bij kamertemperatuur. De realisatie van het toepassen van BFO hangt af van het verhelpen van uitdagingen met betrekking tot groei van BFO dunne films en de functionele eigenschappen daarvan. Daarom is dit proefschrift gericht op het ontrafelen van wetenschappelijke kwesties omtrent de groei van BFO dunne films door het modifieren van het raakvlak met het onderliggende substraat, wat controle over formatie van specifieke domeinen mogelijk maakt. De functionele eigenschappen worden dus bestudeerd met een focus op de variatie in geleidend gedrag.

In hoofdstuk 2 wordt getoond dat de oppervlakterminatie van SrTiO_3 (STO) substraten de groeikinetic van BFO dunne films verandert. Een B-vlak getermineerd

(TiO_2 atoomvlak) STO oppervlak leidt tot BFO dunne film groei met een grote nucleatiedichtheid, resulterend in vorming van alle structurele domeinvarianten van BFO, waarbij enkele defecten zichtbaar zijn op het oppervlak van de dunne film. Aan de andere kant faciliteert een A-vlak getermineerd (SrO atoomvlak) STO oppervlak op stap-vloei gelijkende BFO dunne film groei door een verhoogde diffusiviteit aan het oppervlak. Dit resulteert in een toename van de invloed van de stapranden van het substraatoppervlak op de BFO dunne film groei en leidt tot selectiviteit onder de structurele domeinvarianten. BFO dunne films op A-vlak getermineerd STO bestaan uit twee structurele domeinvarianten met domeinen die geordend zijn over een groter gebied vergeleken met BFO dunne films op B-vlak getermineerde STO substraten.

Het bestuderen van de effecten van het raakvlak is uitgebreid van oppervlakterminatie naar oppervlaksymmetrie in hoofdstuk 3. BFO dunne films die gegroeid zijn op TbScO_3 (TSO) $(110)_o$ en $(001)_o$ substraten vertonen het bestaan van verschillende structurele varianten met significante variatie in formatie van domeinen en domeinwanden. Op beide substraten worden voornamelijk twee structurele varianten van verschillende paren geselecteerd door verschillende symmetriedoorbrekende parameters. TSO $(110)_o$ substraten bevorderen vooral de formatie van neutrale 109° domeinwanden met erg kleine domeinbreedtes. Selectiviteit in structurele varianten ontstaat door de niet- 90° hoek welke gepositioneerd is langs de richting loodrecht op het TSO $(110)_o$ substraat. Aan de andere kant bevorderen TSO $(001)_o$ substraten de formatie van geladen 109° domeinwanden in een meanderende vorm. In dit geval komt de selectiviteit in structurele varianten door het feit dat de niet- 90° hoeken evenwijdig aan het substraatoppervlak vlak liggen. Verschillen tussen de BFO films op TSO $(110)_o$ en $(001)_o$ substraten tonen duidelijk dat het effect van substraten niet gelimiteerd is tot mechanische spanning, wat vaak beschouwd wordt als het grootste effect, maar dat substraatsymmetrie een cruciale rol speelt in de groei van BFO dunne films.

Succesvol toepassen van BFO hangt sterk af van de elektrische eigenschappen. Daarom is hoofdstuk 4 gewijd aan de studie van de geleidende eigenschappen van BFO dunne film stapelingen. Twee invloed hebbende aspecten worden beschouwd, namelijk de elektrodelaaag en de terminatie van het oppervlak. $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) en Nb gedoteerd STO (Nb:STO) zijn als elektroden gebruikt. Er wordt getoond dat een lagere Schottky barrière aanwezig is aan het LSMO-BFO raakvlak vergeleken met het Nb:STO-BFO raakvlak. Daarom is een hogere geleiding waargenomen in BFO stapelingen met LSMO elektrodelagen. Voor de betreffende variatie in oppervlakte terminatie is het verschil tussen Schottky barrière waarden aan het A-vlak LSMO-BFO en B-vlak LSMO-BFO erg klein. In tegenstelling daarmee is de Schottky barrière waarde aan het A-vlak Nb:STO-BFO bijna twee keer de waarde aan het Nb:STO-BFO raakvlak. Raakvlakmodificatie in BFO dunne film stapelingen

geeft mogelijkheid tot controle over de Schottky barrière aan het raakvlak, zodat problemen omtrent elektrische lekkage voorkomen kunnen worden.

Een van de meest controversiële onderwerpen omtrent BFO dunne film eigenschappen is de domeinwandgeleiding. Hoofdstuk 5 presenteert de resultaten van metingen aan de domeinwand geleiding in BFO dunne films op Nb:STO en TSO (001)_o substraten. In BFO/Nb:STO monsters worden niet-stochastische veranderingen in stroom waargenomen tijdens stroom-spanning metingen. Beweerd wordt dat dit komt door zuurstofvacatures die zich op willekeurige posities in de energieband bevinden. Bovendien worden positieve polarisatie ladingen verantwoordelijk gehouden voor het verzamelen van zulke zuurstofvacatures in de nabijheid van kop-aan-kop 109° domeinwanden in BFO dunne films op TSO (001)_o substraten. Dit leidt tot het ontstaan van preferentiële domeinwandgeleiding in BFO dunne films.

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